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BULLETIN

OF THE

CHEMICAL SOCIETY OF JAPAN

Vol. 33 No. 10 October 1960

JAN 5 1961

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Published by the Chemical Society of Japan

THE CHEMICAL SOCIETY OF JAPAN
(NIPPON KAGAKUKAI)

Founded in 1948

Successor to the former Chemical Society of Japan founded in 1878 and to the Society of Chemical Industry, Japan founde in 1898.

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN

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Isomerization of Unsaturated Fatty Acids and their Esters with Acetic or Inorganic Acid

By Yutaka WATANABE

(Received January 18, 1960)

It is generally accepted, that the isomerization of fatty materials includes the following events:

i) Formation of conjugated double bonds in the fatty molecule by heating with alkali; that gives rise to cis → trans isomerization[1].

ii) Shifting of double bonds during catalytic hydrogenation[2].

iii) Elaidinization with selenium or nitrous acid[3].

There are many literatures which describe the reaction of unsaturated fatty materials with concentrated sulfuric acid[4], and a synthesis of hydroxy acids or production of sulfated or sulfonated oils and of "iso-oleic" acid was also given. But no detailed description of analysis of "iso-oleic" acid was shown in previous literatures. Furthermore, it is not possible to find any information which refers to the reaction of unsaturated fatty materials with aqueous sulfuric acid solution at moderate temperatures.

Besides these matters the author[5] found the isomerization of oleate or palmitoleate of the following scheme, followed by oxidative fission with *tert*-butyl chromate (type C)*:

$$CH_3(CH_2)_mCH : CH(CH_2)_7C\begin{matrix}O\\ \diagdown\\ \diagup\\ OCH_3\end{matrix}$$

$$\longrightarrow CH_3(CH_2)_nCH : CHC\begin{matrix}O\\ \diagdown\\ \diagup\\ OCH_3\end{matrix}$$

$m=7$ or 5; $n=14$ or 12

In this experiment, when methyl oleate in benzene was oxidized with *tert*-butyl chromate (type C) at 40°C for 30 hr., nonanoic, azelaic and palmitic acids were obtained as oxidation products. On the other hand, it was found, that oleate in benzene/acetic acid or benzene/acetic acid/sulfuric acid was isomerized partly into 2-octadecenoate. In the oxidation of palmitoleate under almost the same condition as that of oleate, the author recognized the formation of myristic, lauric, capric, heptanoic and azelaic acid. From these experimental results, he proposed the β-oxidative action of *tert*-butyl chromate, accompanied by the isomerization shown in the above scheme.

It seems very noticeable that the isomerization of unsaturated fatty materials in acid medium proceeds even at moderate temperature. From this point of view, the action of acetic acid and inorganic acids, including aqueous sulfuric, phosphoric and boric acids, towards sesame oil fatty acid was studied. It was observed that the isomerization (conjugation) of triethylenic fatty acids of sesame oil constituents occurs by the treatment of above reagents except boric acid. The examination of ultraviolet absorption spectra of fatty acid was convenient for this purpose.

Experimental

Sample.—*Methyl Oleate*[6].—Commercial olive oil was saponified with alcoholic potash, and the mixed fatty acids obtained were treated by means of lead salt-alcohol method. The resulted liquid acid had an iodine value of 93.1, and a 10% solution of this acid in acetone was cooled to −20°C and filtered. The cake of oleic acid was collected after maintaining the filtrate at −60°C. This acid (I. V. 90.1) was esterified in the usual manner, and the ester obtained was distilled under reduced pressure. Methyl oleate thus prepared had the following properties: b. p.$_5$ 180°C; d_4^{25} 0.8712; n_D^{25} 1.4469; acid value 0.17; saponification value 183.9; I. V. 86.4.

Ozonization of this oleate in chloroform gave no palmitic acid. This indicates the absence of 2-octadecenoate in the specimen.

Methyl Palmitoleate.—Sperm oil fatty acid was fractionated into solid and liquid acid by means of lead salt-alcohol method. The liquid acid obtained was esterified and the ester was distilled in vacuo. Methyl palmitoleate thus obtained had the following properties: b. p.$_4$ 160~165°C; d_4^{25} 0.8748; n_D^{25} 1.4481; A. V. 3.45; S. V. 201.5; I. V. 86.1. Ozonolysis of this palmitoleate gave a complex mixture

1) R. T. Holman, W. O. Lundberg and T. Malkin ed., "Progress in the Chemistry of Fats and Other Lipids", Vol. 4, Pergamon Press, London (1957), p. 227.

2) A. E. Bailey, "Industrial Oil and Fat Products", 2nd ed., Interscience Publishers, New York (1951), p. 687.

3) A. E. Bailey, ibid., p. 910.

4) For instance, R. M. Koppenhoefer, *J. Am. Leather Chem. Assoc.*, **34**, 622 (1939); T. N. Mehta et al., *J. Indian Chem. Soc. Ind. & News Ed.*, **15**, 111 (1952); **16**, 81 (1953); **18**, 195 (1955); K. Nishizawa et al., *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **34**, 836 (1927); **49**, 12 (1946).

5) Y. Watanabe, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 310 (1959); ibid., **80**, 1187 (1959).

* *tert*-Butyl chromate (type C) was prepared according to the method of Oppenauer and Oberrauch (*Anal. asoc. quim. Argentina*, **37**, 247 (1949)).

6) E. G. Ball ed., "Biochemical Preparations", Vol. 2, Wiley, New York (1952), p. 100.

of saturated monocarboxylic acids. Paper chromatographic analysis of the mixed acids, according to the method of Inouye et al.[7] gave the result that the major components of this mixture were nonanoic and heptanoic acids, and the minor were myristic and capric (trace) acids. This means, therefore, that palmitoleate contains a small amount of oleate and a trace of myristate and caprate as contaminants. Ultraviolet and infrared absorption spectra of palmitoleate revealed, that there is neither conjugated diethylenic and more highly conjugated polyethylenic acid esters nor trans type acid esters in the sample.

Sesame Oil Fatty Acid. — Saponification of commercial sesame oil (d_4^{25} 0.9097; n_D^{25} 1.4718; A. V. 0.14; S. V. 187.7; I. V. 118.9; unsaponifiable matter 1.11%) with alcoholic potash, gave the mixed fatty acids. This had the following properties: d_4^{25} 0.8983; n_D^{25} 1.4627; A. V. 185.0; I. V. 120.0; content of conjugated diene 0.55%; conjugated triene 0%. Ultraviolet absorption spectrum of this mixed acids is shown in Fig. 1. The content of linoleic and linolenic acids in this sesame oil fatty acid, estimated by the A. O. C. S. standard method[8], was 20.0 and 14.2%, respectively.

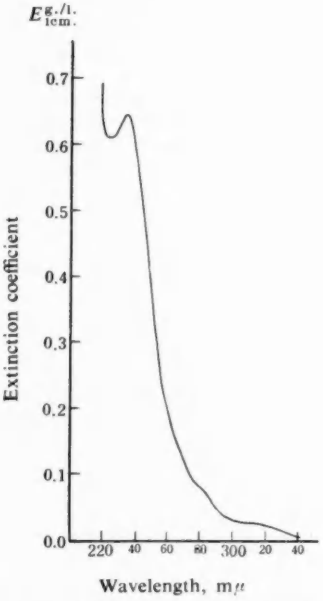


Fig. 1. U. V. absorption spectrum of sesame oil fatty acid.

Ultraviolet and Infrared Absorption Spectrum. — All ultraviolet and infrared absorption spectra mentioned in the present paper were measured by using Hilger's UVISPEK and H-800 spectrophotometer, respectively.

Purified ethyl alcohol was used as a solvent for ultraviolet spectroscopy instead of isoöctane.

Isomerization of Double Bond to α,β-Conjugated Position to Ester Carbonyl Group[5]. — *Methyl Oleate.* — Twenty grams of methyl oleate were added to the mixture of 90 g. of benzene, 36 g. of *tert*-butyl alcohol, 15 g. of acetic acid, and 3.0 g. of acetic anhydride, and the whole was kept at 40°C for 30 hr. with stirring. On the other hand, the mixture of 8 g. of oleate, 26 g. of benzene, 12 g. of acetic acid and 0.1 g. of concentrated sulfuric acid was kept at 70°C for 20 hr. with stirring. After each reaction time mentioned above was over, the reaction mixture was washed with water, 3% aqueous sodium bicarbonate solution, and finally again, water successively dried over anhydrous sodium sulfate, and a mixture of fatty esters was recovered after distilling off the volatile materials.

The fatty esters thus obtained were ozonized at 0°C using chloroform as a solvent. A mixture of monocarboxylic acids was obtained after the oxidative decomposition of the ozonized material, followed by extraction with petroleum ether. Paper chromatographic analyses of samples, derived from different isomerization condition were carried out using the same method as mentioned above. It was recognized that the chromatogram showed the presence of two kinds of fatty acid, namely nonanoic (major) and palmitic (minor) acids. When the mixtures of both of the monocarboxylic acids were fractionally crystallized from methyl alcohol at 0°C, an acid (m. p. 60~63°C) was precipitated in each case. This acid was identified as palmitic acid by the preparation of its *p*-bromophenacyl ester (m. p. 84~84.5°C) and mixed melting point determination with the known specimen.

Methyl Palmitoleate. — Eight grams of methyl palmitoleate were added to the mixture of 32 g. of benzene and 5.4 g. of acetic acid, and the whole was kept at 70°C for 30 hr. with stirring. The reaction product was treated in a similar way as in the case of oleate, and the result obtained was as follows. Monocarboxylic acids obtained were heptanoic, nonanoic, capric (trace) and myristic acids. The amount of myristic acid in this case seemed to be larger than that of the sample derived from the starting material (palmitoleate itself); because, the larger and more intense spot of myristic acid on the paper chromatogram was observed in the case of isomerized sample than in the case of the starting material although almost the same quantity of each sample was analyzed by means of paper chromatography mentioned above. However, the conclusive evidence, that the amount of myristic acid increased after isomerization followed by ozonization was not so remarkable.

Formation of Conjugated Triethylenic Acid in Sesame Oil Fatty Acid. — *Blank Test.* — Fifteen grams of sesame oil fatty acid and 80 g. of water in a flask provided with a gas-inlet tube, a stirrer, and a reflux condenser, were maintained at 90°C with constant stirring, under nitrogen atmosphere, for 3~30 hr. Contents of conjugated diene and triene in samples calculated from the equation shown in standard method were shown in Table I.

7) Y. Inouye, O. Hirayama and M. Noda, *Bull. Agr. Chem. Soc. Japan*, **20**, 200 (1956); *J. Agr. Chem. Soc. Japan (Nippon Nogei-kagaku Kaishi)*, **31**, 568 (1957).

8) American Oil Chemists' Soc., Tentative Method Cd 7-48; *J. Am. Oil Chemists' Soc.*, **35**, 593 (1958).

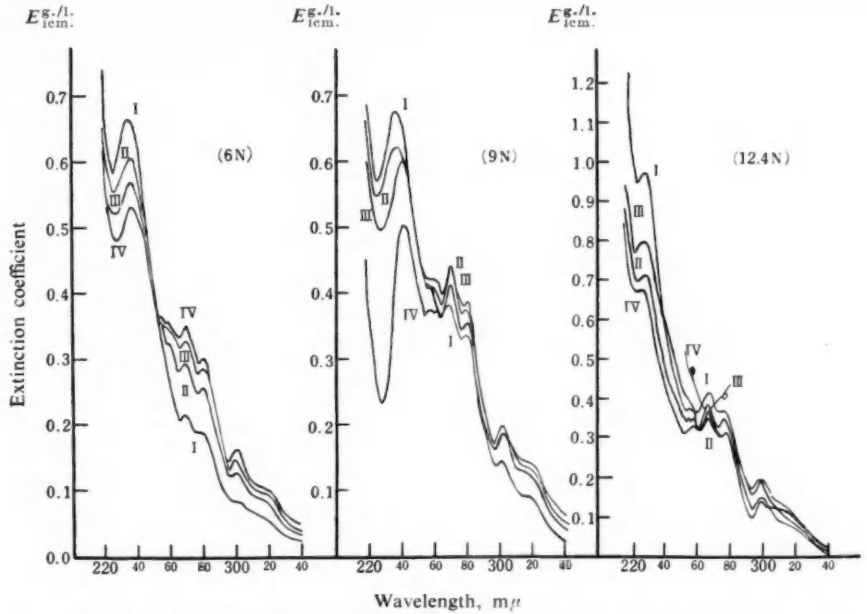


Fig. 2. U. V. absorption spectra of sesame oil fatty acid isomerized with aqueous sulfuric acid solutions. I 3 hr., II 10 hr., III 20 hr., IV 30 hr.

TABLE I. CONTS. OF CONJUGATED DIENE AND TRIENE (BLANK TEST)

Time, hr.	3	10	20	30
Diene, %	0.70	0.89	1.17	1.79
Triene, %	0	0	0.0026	0.0026

Aqueous Sulfuric Acid Solution.—The concentrations of sulfuric acid solutions used for isomerization were 6 N (d=1.18), 9 N (d=1.26) and 12.4 N (d=1.35), respectively. Each time, 30 g. of sesame oil fatty acid and 300 g. of aqueous sulfuric acid solution were treated similarly as in the case of the blank test. These isomerization experiments were carried out at 90°C. After each reaction time (Table II), fatty acid was taken out from the reaction vessel, and washed thoroughly with water and dried, and the ultraviolet absorption spectrum (Fig. 2) was measured, and the contents of diene and triene in it were calculated. The results were shown in Table II.

TABLE II. CONTS. OF CONJUGATED DIENE AND TRIENE (TREATMENT WITH SULFURIC ACID SOLUTION)

Time, hr.		3	10	20	30
	Concn. of aq. H_2SO_4				
Diene, %	6 N	0.54	0.48	0.45	0.42
	9 N	0.55	0.50	—	—
Triene, %	6 N	0.010	0.056	0.039	0.052
	9 N	0.053	0.062	0.086	0.085
	12.4 N	0.062	0.062	0.072	0.084

When sesame oil fatty acid was treated with 6 N sulfuric acid at room temperature for 30 hr., no remarkable change of the ultraviolet absorption spectrogram was observed.

Phosphoric Acid. — Phosphoric acid (300 g.) and sesame oil fatty acid (60 g.) were treated quite similarly as in the case of sulfuric acid solution at 90°C. In this case, remarkable coloration of phosphoric acid was observed during the reaction. After the reaction, the fatty acid was recovered similarly as in the case of sulfuric acid solution. The results obtained were shown in Table III. Ultraviolet absorption spectra of isomerized acids were shown in Fig. 3. Physical properties of recovered fatty acids were shown in Table IV.

TABLE III. CONTS. OF CONJUGATED DIENE AND TRIENE (TREATMENT WITH PHOSPHORIC ACID)

Time, hr.	3	6	10	15	20	30
Diene, %	0.61	0.65	0.62	0.76	0.61	0.71
Triene, %	0.0619	0.0711	0.0776	0.1066	0.0882	0.1040

TABLE IV. PHYSICAL PROPERTIES OF ISOMERIZED SESAME OIL FATTY ACID AFTER TREATMENT WITH PHOSPHORIC ACID AT 90°C

Time, hr.	d_4^{25}	n_D^{25}	A. V.	I. V.
3	0.8924	1.4636	185.1	117.2
15	0.8920	1.4632	186.6	118.9
30	0.8936	1.4630	188.8	117.3

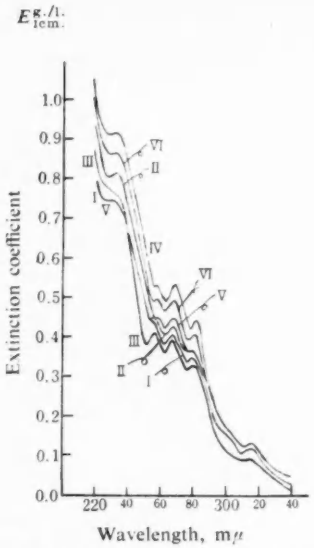


Fig. 3. U. V. absorption spectra of sesame oil fatty acid isomerized with phosphoric acid.
I 3 hr., II 6 hr., III 10 hr., IV 15 hr., V 20 hr., VI 30 hr.

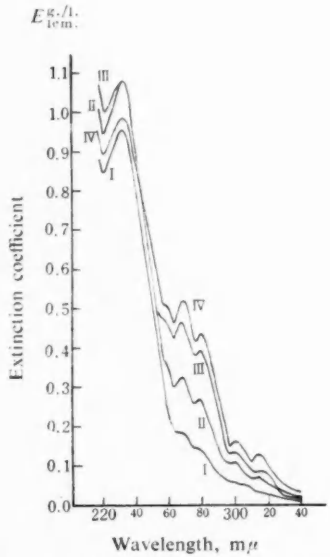


Fig. 4. U. V. absorption spectra of sesame oil fatty acid isomerized with acetic acid.
I 3 hr., II 10 hr., III 20 hr., IV 30 hr.

Glacial Acetic Acid. — Glacial acetic acid (300 g.) and sesame oil fatty acid (30 g.) were mixed and the solution was maintained at 90°C under nitrogen atmosphere, with stirring, for 30 hr. In the course of the reaction, 30 cc. portion of the solution was taken out, poured into water, extracted with ether and the ethereal solution was washed thoroughly with water, and dried over anhydrous sodium sulfate. After evaporation of the solvent, isomerized material was recovered, and its ultraviolet absorption spectrum was measured (Fig. 4). The contents of conjugated diene and triene calculated were shown in Table V.

TABLE V. CONTS. OF CONJUGATED DIENE AND TRIENE (TREATMENT WITH GLACIAL ACETIC ACID)

Time, hr.	3	10	20	30
Diene, %	0.78	0.88	0.88	0.81
Triene, %	0.0066	0.054	0.096	0.112

Treatment with Boric Acid. — At 90°C, sesame oil fatty acid (30 g.), boric acid (90 g.) and water (410 g.) were treated similarly as in the case of the blank test. Even after 30 hr., the fatty acid was so stable that the contents of conjugated diene and triene in it were essentially the same as in the case of the blank test.

Discussion

It will be noticeably demonstrated that the isomerization of unsaturated fatty materials occurs at moderate temperature (30~90°C) in the acid medium mentioned above. In the case of monoethylenic fatty esters, namely methyl oleate and palmitoleate, the double bond migrates to α,β-conjugated position to ester carbonyl group. Although the isolation of isoöleate or isopalmitoleate was unsuccessful, the formation of α,β-unsaturated esters was definitely supported by the identification of a shorter-chain saturated fatty acid, which was obtained after ozonolysis of isomerized products. The identification of palmitic and myristic acids has important meaning in this aspect. These facts support the β-oxidation mechanism of oleate and palmitoleate with *tert*-butyl chromate (type C).

In the case of sesame oil fatty acid, it is sure, that conjugation of triethylenic system in fatty acid molecule proceeds, when it was treated with acetic, phosphoric or aqueous sulfuric acid solution at 90°C. But there was no appreciable formation of a conjugated diethylenic system in such treatment, because the contents of conjugated diene of sesame oil fatty acid were almost constant throughout the whole various conditions. It is certain that the formation of conjugated triethylenic acid proceeds neither in the experiment of the blank test nor with the treatment with boric acid at 90°C. Also, the same result was obtained in the case of the treatment with 6 N sulfuric acid at room temperature. The smallest content found (0.0066%) of conjugated

triene was obtained in the treatment of the fatty acid with acetic acid at 90°C for 3 hr. The highest content observed (0.112%) was obtained in the isomerization with acetic acid at 90°C for 30 hr. This value (0.112%) corresponded to 0.784% for linolenic acid present in sesame oil fatty acid.

According to Privett and Quackenbush[9], no phosphorylation occurred, when ethyl linoleate was treated with a catalytic amount of phosphoric acid (below 1%) in a sealed tube, under vacuum at 100°C for 36 hr. They have refered nothing to the isomerization of linoleate. However, in the case of the treatment of fatty acid with a large amount of phosphoric acid at 90°C described in the present paper, the author recognized the isomerization of fatty acid as above. But the physical properties of the isomerized products shown in Table IV seemed to be virtually constant, the same interpretation as for no phosphorylation can be relied on.

The author wishes to express his gratefulness to Professor T. Matsuura for his suggestions and encouragement, and also to Messrs. H. Tanimoto and A. Ohtawa for their assistance.

Department of Chemistry
Faculty of Science
Hiroshima University
Hiroshima

9) O. S. Privett and F. W. Quackenbush, *J. Am. Oil Chemists' Soc.*, **31**, 225 (1954).

*Studies on Organic Peroxides. VI. Thermal Analysis of the Decomposition of Benzoyl Peroxide by Ferrous Ion**

By Shigeo HASEGAWA, Norio NISHIMURA and Kimpei MIURA

(Received February 11, 1960)

In the previous paper[1], the analytical method was applied to follow the rate of the decomposition of benzoyl peroxide catalyzed by ferrous ion and it was found that the apparent decomposition rate was of the first order with respect to the concentration of benzoyl peroxide and that the activation energy of the decomposition was about 14 kcal./mol. This was much less than that of the spontaneous decomposition. In this report, similar reactions were carried out in methanol, ethanol, *n*-propanol and *n*-butanol and the reaction was followed by means of the method of thermal analysis[2].

Experimental

Reagents.—Benzoyl peroxide and ferrous chloride were prepared by the methods reported earlier[3]. Other chemicals used were of reagent grade and repeatedly distilled.

Apparatus and Procedure.—The reaction was carried out in a glass calorimeter shown in Fig. 1. In this figure, A is a Dewar vessel, the capacity of which is about 200 cc., B a glass stirrer sealed by mercury, C a Beckmann thermometer, D a platinum wire heater, E a glass vessel of about 30 cc. and F and F′ glass tubes.

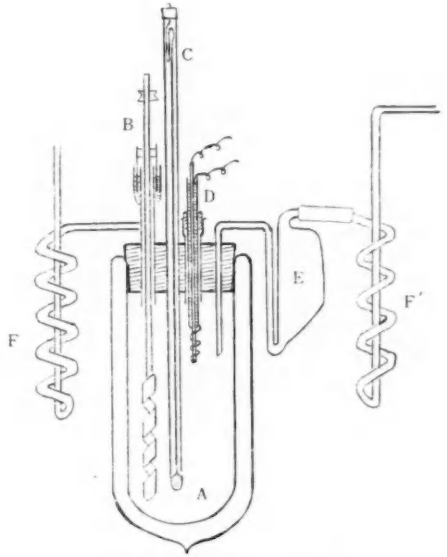


Fig. 1. Reaction vessel.

* Presented in part at the Chugoku-Shikoku and Kinki Local Meeting of the Chemical Society of Japan, Tokushima, August 29 (1958).

1) S. Hasegawa and N. Nishimura, This Bulletin, **33**, 775 (1960).

2) S. Horiba and T. Ichikawa, *Rev. Phys. Chem. Japan*, **1**, 145 (1927); Ichikawa, *Z. Physik. Chem.*, (B) **10**, 299 (1930).

3) S. Hasegawa et al., This Bulletin, **31**, 696 (1958).

The atomosphere of the vessel was previously substituted by carbon dioxide. Oxygen-free benzoyl peroxide and ferrous chloride solutions were introduced into A and E, respectively. The calorimeter was held in a thermostat. The temperature in A was adjusted to that of the thermostat by the heater D. After thermal equilibrium was attained, the ferrous chloride solution in E was siphoned into A. As soon as they were mixed, the reaction started and the rise of the temperature was recorded as the time passed.

The initial concentration of benzoyl peroxide was 0.01 mol./l. for all runs.

The Method of Thermal Analysis.—The fundamental equation of thermal analysis is given by Eq. 1[2,4],

$$\frac{dT}{dt} + K\Delta T = \frac{Q}{W} \cdot \frac{dx}{dt} \qquad (1)$$

where dT/dt is the velocity of temperature change in solution, and $K\Delta T$ is a correction term for Newtonian cooling due to the temperature difference ΔT between the system and its surroundings and hence the rise in the temperature of reaction solution, K being the cooling constant. Q and W denote the heat of the reaction and the water equivalent of the reaction vessel, respectively, and dx/dt the rate of the reaction.

The cooling constant K can easily be determined by plotting the temperature difference between the reaction vessel and the thermostat against time.

When a reaction is of the first order, the rate of the reaction may be expressed as:

$$dx/dt = kae^{-kt} \qquad (2)$$

where k is the specific reaction rate and a is the initial concentration of the reactant. From Eqs. 1 and 2, it follows,

$$\log(dT/dt + K\Delta T) = \log\frac{Q}{W} \cdot ka - \frac{kt}{2.303} \qquad (3)$$

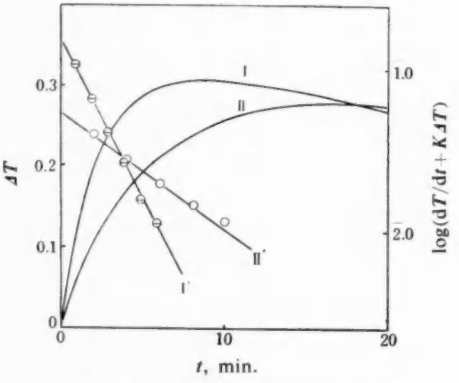


Fig. 2. Curves I and II: ΔT vs. t; curves I' and II': $\log(dT/dt+K\Delta T)$ vs. t in ethanol at 15°C; $[FeCl_2]_0$: 0.0038 mol./l. for I and 0.0012 mol./l. for II, respectively; $[BPO]_0$: 0.01 mol./l.

4) E. Suito, *Rev. Phys. Chem. Japan*, **13**, 74 (1939).

Accordingly, the plot of the left hand side of Eq. 3 against time t will give a straight line, the slope of which is $k/2.303$.

Results

The ferrous ion catalyzed decomposition of benzoyl peroxide is a exothermal reaction and an example is shown in Fig. 2 in which curves I and II show the dependence of ΔT upon

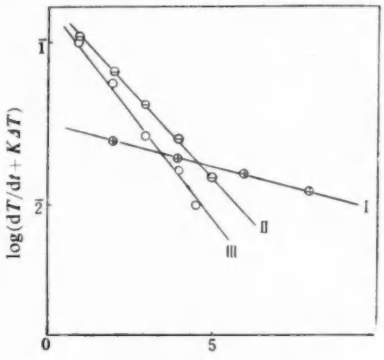


Fig. 3. $\log(dT/dt+K\Delta T)$ against t.
I: methanol, 40°C, $[FeCl_2]_0$: 0.0050 mol./l.
II: butanol, 15°C, $[FeCl_2]_0$: 0.0030 mol./l.
III: propanol, 15°C, $[FeCl_2]_0$: 0.0030 mol./l.
$[BPO]_0$: 0.01 mol./l.

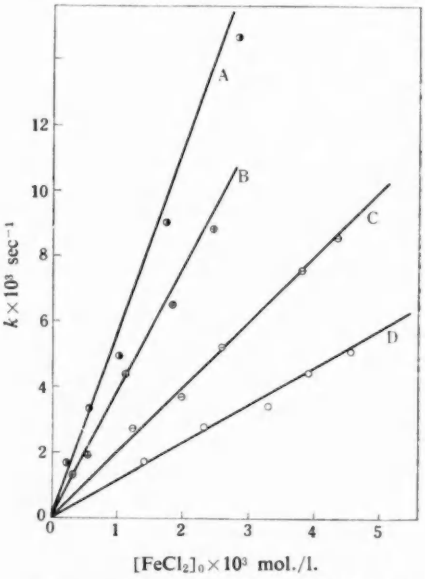


Fig. 4. Dependence of k upon $[FeCl_2]_0$ in ethanol at various temperatures: A, 30; B, 25; C, 15; D, 10°C, respectively; $[BPO]_0$: 0.01 mol./l.

TABLE I. THE RATE CONSTANTS FOR THE DECOMPOSITION OF BENZOYL PEROXIDE BY FERROUS ION

Temp. °C	$[FeCl_2]_0 \times 10^3$ mol. l^{-1}	$k \times 10^3$ sec^{-1}	k' l. mol^{-1} sec^{-1}	k'_{av}
		Methanol		
25	2.00	0.18	0.09	
	3.00	0.29	0.10	0.10 ± 0.00^3
	4.00	0.43	0.11	
	5.00	0.48	0.10	
30	1.90	0.54	0.28	
	3.00	0.69	0.23	0.23 ± 0.01^4
	4.66	0.92	0.20	
	4.90	0.92	0.19	
35	1.50	0.48	0.32	
	2.50	0.84	0.34	0.29 ± 0.02
	3.50	0.98	0.28	
	4.50	1.04	0.23	
40	1.50	1.00	0.67	
	2.74	1.38	0.50	0.54 ± 0.03
	3.50	1.80	0.51	
	5.00	2.34	0.47	
		Ethanol		
10	1.38	1.77	1.28	
	2.31	2.80	1.21	
	3.30	3.45	1.05	1.16 ± 0.03
	3.92	4.49	1.15	
	4.54	5.14	1.13	
15	1.22	2.76	2.26	
	1.99	3.76	1.89	
	2.59	5.26	2.03	2.03 ± 0.04
	3.81	7.60	1.99	
	4.3[5]	8.56	1.97	
25	0.29	1.34	4.62	
	0.53	1.92	3.62	
	1.11	4.41	3.97	3.87 ± 0.13
	1.83	6.52	3.56	
	2.45	8.83	3.60	
30	0.23	1.65	7.08	
	0.55	3.34	6.07	
	1.00	4.91	4.91	5.70 ± 0.27
	1.71	8.98	5.25	
	2.82	14.66	5.20	
		n-Propanol		
5	0.96	1.42	1.48	
	2.39	3.30	1.38	
	3.08	3.65	1.18	1.34 ± 0.05
	3.82	5.76	1.51	
	5.00	5.83	1.17	
10	1.28	3.22	2.52	
	2.17	5.37	2.48	
	2.92	6.72	2.30	2.44 ± 0.04
	4.00	10.48	2.62	
	5.04	11.55	2.29	
15	1.00	3.84	3.84	
	2.00	7.22	3.61	
	3.00	10.36	3.45	3.44 ± 0.10
	4.00	13.43	3.36	
	5.00	14.58	2.92	
		n-Butanol		
5	1.04	1.80	1.73	
	2.10	2.92	1.39	
	3.08	3.88	1.26	1.38 ± 0.06
	3.98	5.07	1.27	
	5.20	6.49	1.25	
10	1.00	2.23	2.23	
	2.00	3.84	1.92	
	3.00	5.53	1.84	2.02 ± 0.05
	4.00	7.98	2.00	
	5.00	10.75	2.15	
15	1.00	2.92	2.92	
	2.00	6.64	3.32	
	3.00	8.83	2.94	3.01 ± 0.08
	3.52	10.94	3.13	
	4.00	12.47	3.11	
	5.00	13.05	2.61	

time t in ethanol at 15°C. The slope dT/dt of the curve at any time t can be obtained from the figure. Curves I′ and II′ which are obtained by plotting the left hand side term in Eq. 3 against time give straight lines, therefore, it may be concluded that this reaction is apparently of the first order. Reactions in methyl, *n*-propyl and *n*-butyl alcohols were also the case, as shown in Fig. 3.

It was also found that the slope of the $\log (dT/dt + K_1 T)$ vs. t curve was independent of the initial concentration of benzoyl peroxide.

According to Eq. 3, the slope of the line should give $k/2.303$. However, the specific rate constant k thus obtained in this reaction can not be considered as the true rate constants, because the ferrous ion may be considered to take part in the reaction. The discussion will be undertaken shortly.

The initial concentrations of the ferrous ion, alcohols and the values of k at various temperatures are listed in Table I. From the table, it may be concluded that the values of k seem directly proportional to the initial concentration of the ferrous ion. For example, k vs. $[FeCl_2]_0$ was plotted at temperatures between 10 and 30°C in ethanolic solution as shown in Fig. 4. It seems that each of the values falls on a straight line and converges to the origin. If this conclusion is correct, it follows:

$$k = k' [FeCl_2]_0 \qquad (4)$$

where k' is a constant. In the fourth and fifth columns in Table I are listed the values of k' calculated from Eq. 4. The slopes in Fig. 4 represent the average values of k' for each temperature.

It may be seen that the differences in the reaction rates among ethanol, *n*-propanol and

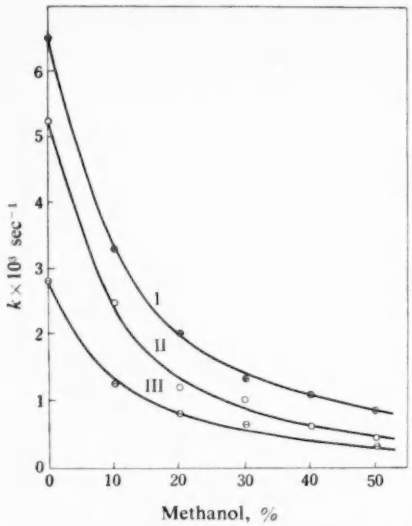


Fig. 5. Values of k for methanol-ethanol mixture: I, 20; II, 15; III, 10°C; $[BPO]_0$: 0.01 mol./l., $[FeCl_2]_0$: 0.0025 mol./l.

n-butanol are not particularly appreciable, but in methanol, the rate is appreciably smaller than in the three other alcohols. In the mixture of methanol and ethanol, k values were rapidly decreased by increasing the proportion of methanol as seen in Fig. 5. Above 50% of methanol, the reaction rates became too small to determine over the experimental temperature range.

Reaction Mechanism

As suggested in the previous paper[1], the overall reactions in this system will take place as follows:

First of all, reaction between benzoyl peroxide and ferrous ion will occur:

$$Fe^{2+} + P \xrightarrow{k_1} RCOO\cdot + RCOO^- + Fe^{3+} \quad (5)$$

The benzoxy radical thus produced will attack a solvent molecule and abstract a hydrogen atom on α-carbon atom.

$$RCOO\cdot + R'CH_2OH \xrightarrow{k_2} RCOOH + R'\dot{C}HOH \quad (6)$$

In addition, the reduction of ferrous to ferric ion is assumed:

$$R'\dot{C}HOH + Fe^{3+} \xrightarrow{k_3} RCHO + Fe^{2+} + H^+ \quad (7)$$

Therefore, the heat evolved in this reaction may be the sum of the contribution from these reactions. Hence, the apparent rate constant k may be considered to include some specific rate constants.

In the previous paper, it was also mentioned that the rate of the decomposition of benzoyl peroxide might well be expressed as

$$-d[P]/dt = k_1[P][Fe^{2+}] \quad (8)$$

In addition, the apparent overall decomposition rate was approximately of the first order, that is

$$-d[P]/dt = k_0[P] \quad (9)$$

where k_0 is a constant. Therefore, the ferrous ion concentration should be constant during the reactions, if Eqs. 8 and 9 are not inconsistent with each other. From Eqs. 8 and 9, it follows,

$$k_0 = k_1[Fe^{2+}] \quad (10)$$

As was assumed, if the rate of reduction of ferric to ferrous ions are equal or almost equal to that of oxidation, the equilibrium between ferrous and ferric ions would be attained. Then, ferrous ion concentration may be expressed in terms of its initial concentration and the equilibrium constant K_0, i.e.,

$$[Fe^{2+}] = \frac{K_0}{1+K_0}[Fe^{2+}]_0 \quad (11)$$

Inserting this value into Eq. 10, it follows,

$$k_0 = k_1 \cdot \frac{K_0}{1+K_0} \cdot [Fe^{2+}]_0 \quad (12)$$

Thus, as was suggested, in the previous paper, k_0 should be a linear function of $[Fe^{2+}]_0$. Eq. 9 shows that k_0 can be obtained from the slope of the $\log[P]$ vs. t curve. If Eq. 12 is compared with Eq. 4, the conclusion that the rate constant k obtained from the thermal analysis is a linear function of the initial ferrous ion concentration, agrees formally with the conclusion that the apparent first order rate constant k_0 obtained from the analytical data, would be a linear function of the initial ferrous concentration. Each value of k and k' could, therefore, be referred as a measure of k_0 and k_1, respectively. Thus, it may be concluded that though the data from the thermal analysis in this reaction do not offer true rate constants, they still offer a means for studying the mechanism of this reaction in alcohols.

Solvent Effect

Since k' corresponds to the true rate constant k_1 as mentioned above, it is of interest to calculate the apparent activation energy by plotting $\log k'$ against $1/T$. The Arrhenius plots may be seen in Fig. 6. By applying the least squares method, the activation energies and the frequency factors for each alcohol were calculated and listed in Table II.

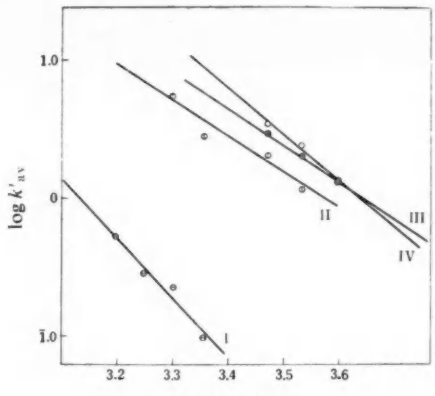


Fig. 6. Plots of $\log k'_{av}$ against $1/T$, solvent, I, methanol; II, ethanol; III, *n*-propanol; IV, *n*-butanol.

TABLE II. ACTIVATION ENERGIES AND FREQUENCY FACTORS

Solvent	E(kcal./mol.)	A	S^*(e. u.) 300°K
Methanol	19.8	3.3×10^{13}	1.3
Ethanol	12.0	2.3×10^{9}	−17.7
n-Propanol	15.0	8.7×10^{11}	−5.9
n-Butanol	12.4	7.5×10^{9}	−15.3
Methanol (10%)-Ethanol (90%)	15.2	3.2×10^{11}	−7.9
Methanol (20%)-Ethanol (80%)	16.7	2.3×10^{12}	−4.0

The influence of the solvent on chemical reaction rate would be partly due to its physical properties such as dielectric constant or molecular size. In reactions between ions and molecules, the solvent will play an important role and the increase in the dielectric constant of the solvent will cause a decrease in the free energy of the system, and hence will result in a decrease in their reaction rates. Since ferrous ions in alcohol are solvated, the reaction rates between ferrous ion and benzoyl peroxide will depend partly on the dielectric constants of the solvents. The dielectric constants of methanol, ethanol, *n*-propanol at 20°C and *n*-butanol at 25°C are 33.7, 25.7, 21.8 and 17.8, respectively[5].

It may be seen from the table that the k' values are increased in the order of methanol, ethanol, *n*-butanol and *n*-propanol, in agreement with the order of decreasing dielectric constants except that the order of *n*-propanol and *n*-butanol is reversed. But the difference in the rates between these alcohols is not so appreciable.

5) International Critical Table, VI, p. 83.

It was pointed out[6] that abstraction of the hydrogen atom from the alcohol molecule took place on the α-carbon atom exclusively.

In reaction 6, methylenic hydrogen atoms will exclusively be abstracted in ethanol, *n*-propanol and *n*-butanol, whereas methyl hydrogen atoms will be abstracted in methanol. This will suggest the exceptionally slow reaction rates in methanol.

Enthalpy-Entropy Relationship

Mention may be made about the relation between activation energy and frequency factor.

There are cases when a linear relationship between ΔS^* and E can be observed. Especially, it was pointed out that in a series of reactions, $\log A$ was a linear function of E when the Hammett equation held[7].

According to the theory of the absolute reaction rates[8], the specific rate constant k of a reaction is related to the standard free energy of activation ΔF^* by Eq. 13:

$$k=\kappa\frac{kT}{h}\exp\left(-\frac{\Delta F^*}{RT}\right) \tag{13}$$

The free energy of activation may be a function of the intensity factors such as steric, resonance, or solvent effects. In a series of reactions, all such intensity factors are assumed to remain constant except that there is a change in one of these intensity factors, and ΔF^* is assumed to be linearly related to it.

Any reaction in the series may be chosen as standard and its specific rate constant may be denoted by k_0. If the difference in the intensity factor between any reaction and the standard one is expressed by $\Delta\chi$, then from the assumption mentioned above, the specific rate constant k can be derived from Eq. 13:

$$\ln k/k_0=-\frac{\Delta\Delta F^*}{RT}=-\frac{1}{RT}\left(\frac{\partial\Delta F^*}{\partial\chi}\right)_T\Delta\chi$$

$$=-\frac{1}{RT}\left\{\left(\frac{\partial\Delta H^*}{\partial\chi}\right)_T-T\left(\frac{\partial\Delta S^*}{\partial\chi}\right)_T\right\}\Delta\chi \tag{14}$$

where $\Delta\Delta F^*$ represents the difference in the standard free energy of activation between the reaction and the standard one; ΔH^* and ΔS^* denote the standard activation enthalpy and entropy, respectively.

In a case when the intensity factor χ represents a substituent effect, the reaction constant

6) M. S. Kharasch, J. L. Rowe and W. H. Urry, *J. Org. Chem.*, **16**, 905 (1951).

7) J. E. Leffler and Shih-Kung Liu, *J. Am. Chem. Soc.*, **78**, 1949 (1956); I. Meloche and K. J. Laidler, ibid., **73**, 1712 (1951); D. A. Brown and R. F. Hudson, *J. Chem. Soc.*, 1953, 883.

8) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes", McGraw-Hill, New York (1941), p. 195.

ρ in the Hammett equation[9] may be expressed as

$$-\frac{1}{RT}\left\{\left(\frac{\partial \Delta H^*}{\partial \chi}\right)_T - T\left(\frac{\partial \Delta S^*}{\partial \chi}\right)_T\right\} = \rho \times \text{const} \quad (15)$$

Jaffé[10] has pointed out, quoting many examples, that in a series of reactions where the Hammett equation held, ρ was linearly related to $1/T$. This fact can successfully be explained by Eq. 15 if $(\partial \Delta H^*/\partial \chi)_T$ and $(\partial \Delta S^*/\partial \chi)_T$ are both independent of temperature.

In a series of related reactions, changes in polarity of a substituted group may be associated with the change in the electrostatic field strength at the reaction center.

Hence it may be reasonable to expect that the greater the enthalpy of activation, the greater will become the entropy of activation, because formation of a more rigid activated complex will need fewer entropy and enthalpy changes and vice versa.

In case of solvent changes, the linear relationship between enthalpy and entropy of activation is also observed[11,12]. If reactants are solvated, solvation will cause the decrease in the potential energy and entropy of the system, and hence both the enthalpy and entropy of activation will be increased. Thus, it may be reasonable to assume that the sign of $(\partial \Delta H^*/\partial \chi)_T$ is the same as that of $(\partial \Delta S^*/\partial \chi)_T$ and that neither of them is zero. Then, there must be a temperature, denoted by β, at which the left hand side of Eq. 14 becomes zero and it must be characteristic in the reaction series. From the discussion mentioned above, it is concluded that at the temperature β, which has been called "isokinetic temperature"[12], all the reaction rates should become identical.

From Eq. 14, it follows:

$$\left(\frac{\partial \Delta H^*}{\partial \chi}\right)_T \Delta\chi = \beta\left(\frac{\partial \Delta S^*}{\partial \chi}\right)_T \Delta\chi \quad (16)$$

or

$$\Delta\Delta H^* = \beta \Delta\Delta S^* \quad (17)$$

where $\Delta\Delta H^*$ and $\Delta\Delta S^*$ denote the difference in the activation enthalpy and entropy between a reaction and the standard one, respectively. Hence, $\Delta\Delta H^*$ is a linear function of $\Delta\Delta S^*$, in agreement with experimental facts.

In this study, the apparent activation energy

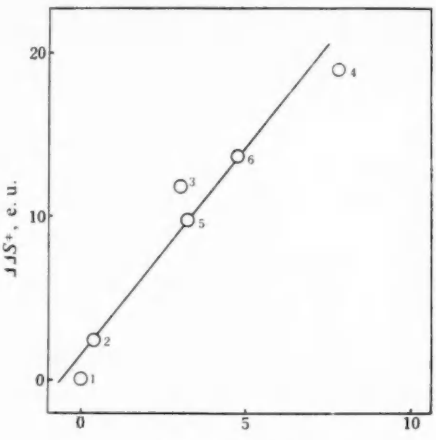


Fig. 7. Relationship between ΔE and $\Delta\Delta S^*$. 1, ethanol; 2, butanol; 3 propanol; 4, methanol; 5, methanol (10%)-ethanol (90%); 6, methanol (20%)-ethanol (80%).

E was also proportional to the activation entropy. In Fig. 7, the reaction in ethanol was chosen as standard, and the differences in activation energies were plotted against the differences in the activation entropies. A straight line was obtained as shown in the figure. From the slope, the isokinetic temperature was calculated to be 400°K.

Summary

The thermal analysis method was applied to follow the rate of the decomposition of benzoyl peroxide catalysed by ferrous ion in methanol, ethanol, *n*-propanol and *n*-butanol.

The apparent rates were of the first order and no fundamental difference in the reaction mechanism was observed among these alcohols. However, the reaction rates in methanol were much slower than in three other alcohols. Solvent effects on the reaction rate were discussed.

Linear enthalpy-entropy relationship was deduced, assuming that the free energy of activation is the linear function of an intensity factor in a series of reactions. This was found to be true in our case.

Department of Chemistry
Faculty of Science
Okayama University
Tsushima, Okayama

9) L. P. Hammett, *J. Am. Chem. Soc.*, **59**, 96 (1937).
10) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).
11) E. A. Moelwyn-Hughes, "The Kinetics of Reactions in Solution", Second Ed., Oxford Univ. Press (1947), p. 278.
12) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

Synthesis and Purification of Sexiphenyl for Scintillator

By Tadashi NOZAKI, Michiko TAMURA, Yuhei HARADA* and Kazuo SAITO

(Received March 21, 1960)

It has been believed that sexiphenyl is an interesting organic semi-conductor and a promising scintillator for charged particles[1]. However its preparation was made only on a small scale[2-4], and an attempt to obtain this compound in sufficient quality and quantity for scintillator met with little success[1]. The present authors have found a favorable condition for the production of 4-nitroterphenyl from *p*-terphenyl (1, 4-diphenylbenzene) and succeeded in obtaining several tens of grams of sexiphenyl in a moderate yield. Although its purification involved a great difficulty, repeated vacuum sublimation and zone refining followed by recrystallization from tetralin afforded this compound in high purity. Its almost colorless single crystal gives an intense violet fluorescence and is satisfactorily used as a scintillator and wavelength shifter for Čerenkov radiation.

Preparation of Sexiphenyl.—The process is shown in Table I. Two methods have so far been presented for the synthesis: 1) the Ullmann condensation of 4-iodoterphenyl with the aid of silver powder at 320°C[2]; 2) the same condensation of a mixture of 4-iodobiphenyl and 4, 4'-diiodobiphenyl with copper powder[3]. According to the present authors' re-examination, both gave a very poor yield. Especially the latter provided a product containing as much as 0.7% iodine, after repeated vacuum sublimation and recrystallization from tetralin and dibutylphthalate. Contrary to the description in the literature, the Ullmann condensation of 4-iodoterphenyl with copper gave a good yield (more than 40%), provided that the iodoterphenyl was sufficiently pure and the condensation was carried out on a small scale. It appears as if the exothermic reaction, when carried out on a large scale, raises the temperature so remarkably that both the yield and the purity of the product were lowered.

4-Iodoterphenyl was obtained from 4-aminoterphenyl hydrochloride by diazotization and Sandmeyer's reaction, made free from phenols and the remaining amines by extraction with xylene and further purified by vacuum distillation and recrystallization from isoamyl acetate. Although both the amine and the diazonium salt are sparingly soluble in dilute hydrochloric acid, the diazotization proceeds in a good yield in suspension. This process compares favorably with that in concentrated sulfuric acid[2].

For obtaining pure 4-aminoterphenyl, preparation of pure 4-nitroterphenyl is essential. Nitration of terphenyl usually gives polynitro

TABLE I. SYNTHESIS OF SEXIPHENYL

Raw material	Product	Process	Remarks
p-terphenyl (I)	4-nitroterphenyl (II) (ca. 60%) 2-nitroterphenyl (15 to 20%) 2'-nitroterphenyl (15 to 25%)	HNO_3 in acetic acid and acetic anhydride	new process
4-nitroterphenyl (II)	4-aminoterphenyl hydrochloride (III) (almost 100%)	$SnCl_2$ in ethanol and HCl	Ref. 2 (slightly modified)
4-aminoterphenyl hydrochloride (III)	4-iodoterphenyl (IV) (ca. 40%)	$NaNO_2$ in HCl suspension; urea and KI	Ref. 2 (modified)
4-iodoterphenyl	sexiphenyl (V) (40 to 80%)	Cu at 280°C	Ref. 2 (modified)

* Present address, Kitazono High School, Itabashi-ku, Tokyo.

1) R. C. Sangstar et al., *J. Chem. Phys.*, **24**, 713 (1956).
2) R. Pummerer and K. Bittner, *Ber.*, **57**, 84 (1924).
3) R. Pummerer and L. Selingsberger, ibid., **64**, 2477 (1931).
4) A. E. Gillam and D. H. Hey, *J. Chem. Soc.*, **1939**, 1170.

compounds[5]. Allen et al. obtained 4-nitroterphenyl in 72% yield in glacial acetic acid in the presence of a small excess of nitric acid[6]; they gave, however, no information on the other 28% portion. The present authors have found that at temperatures exceeding 100°C and in glacial acetic acid containing about 10% of acetic anhydride and a trace of sulfuric acid, the rate of mono-nitration of *p*-terphenyl is significantly greater than the decomposition of nitric acid, which is in turn much greater than the rate of nitration of mononitroterphenyls. Higher temperature and greater concentration of acetic anhydride and sulfuric acid increase the solubility of *p*-terphenyl, but facilitates the decomposition of nitric acid, resulting in incomplete nitration of *p*-terphenyl. On the other hand, the amount and the concentration of nitric acid affected the result to a less extent. When the reaction mixture was cooled, fairly pure 4-nitroterphenyl separated as light yellow needles. Column chromatography of the mother liquor gave pure 2-nitro- and 2'-nitroterphenyl.

Purification of Sexiphenyl.—Crude sexiphenyl obtained by vacuum sublimation from the condensation product was yellow in color and contained significant amounts of copper and iodine. Most copper was removed by digesting the sublimate in aqueous potassium cyanide solution. Extremely low solubility of sexiphenyl in any organic solvent (e.g. less than 0.1 g. in one litre of boiling tetralin) makes recrystallization and chromatographic purification very laborious or even impracticable. It was further disclosed by neutron activation analysis that vacuum sublimation and recrystallization from various organic solvents were less effective for the removal of iodine-containing compounds. On the other hand, a cycle consisting of zone refining and vacuum sublimation was very useful for this purpose. (Table II) It appears as if the iodine-containing substance suffers thermal decomposition during zone refining to give compounds that are more easily removed through these processes. However, too high a temperature caused considerable decomposition of sexiphenyl itself, especially when the purity was low. Since the thermal decomposition of sexiphenyl becomes marked over 480°C, the zone refining was best effected at a maximum temperature between 440 and 450°C.

After a vacuum sublimation and a recrystallization from tetralin, the crystalline product gave the correct carbon and hydrogen content. Nevertheless the melting point rose with repeated zone refining and vacuum sublimation, until it reached a constant value after four times' repetition of the cycle, a recrystallization from tetralin and a vacuum sublimation. The final product becomes a translucent fluid at 428~429°C; it appears to be present in a liquid crystalline state until the translucent phase becomes transparent sharply at 543°C. Further purification brought about no change in these constants. Formation of a nematic or a smectic state is quite probable for such a long molecule. The melting point seems to be very sensitive toward impurity and the low values (465°C[3] and 475°C[2]) given by former authors appear to be due to insufficient purity.

TABLE II. IODINE CONTENT OF SEXIPHENYL PURIFIED BY ZONE REFINING AND VACUUM SUBLIMATION

Repetition of the cycle	Location of sample piece (cm. from the bottom)	I content (p.p.m.)
2	0	6.5
	2	3.0
	4	1.6
	6	5.2
	7.5 (top)	2.0
	residue on sublimation	2.5
4	0	<0.15
	2	<0.08
	4	<0.3
	6	<0.05
	7 (top)	<0.06
5	after recrystaln. and sublimation (final product)	<0.04

The quantity decreased to one sixth of that of the crude compound through the purification process, but the purity was so high that no impurity element was detected by chemical and neutron activation analysis. The low iodine content (less than 0.04 p.p.m.) compares with that of silicon for semi-conductor, which is regarded as one of the purest substance available. The final product is evaporated onto the window of a photomultiplier tube in vacuo and used as wavelength shifter. It is also converted into a large single crystal (10×5×2 mm.) and used as scintillator for alpha- and beta-rays. The photomultiplier pulse obtained with this scintillator is higher than that with quaterphenyl or anthracene, which has been regarded the best organic scintillator. The result will be reported elsewhere together with the optical properties of sexiphenyl.

Experimental

Preparation of Sexiphenyl. — *Mono-nitration of p-Terphenyl.*—Chemically pure *p*-terphenyl (I) (m. p.

5) H. France, I. M. Heilbron and D. H. Hey, *J. Chem. Soc.*, **1938**, 1364.
6) C. F. A. Allen and D. M. J. Burness, *J. Org. Chem.*, **14**, 177 (1949).

205~210°C, 500 g.) was dissolved in a boiling mixture of glacial acetic acid (18 l.) and acetic anhydride (2 l.) containing 6 N sulfuric acid (1 ml.). The solution was cooled to 105°C and treated with small portions of nitric acid (*d*, 1.42; total 200 ml.) with good stirring, the temperature being kept below 110°C. When the evolution of brown gas ceased, the solution was heated to boiling and then cooled to give small pale yellow needles of 4-nitroterphenyl (II), which were recrystallized from isoamyl acetate. M. p. 213°C, yield 290 g., corresponding to 60% of I.

Found: C, 78.46; H, 4.71; N, 5.02. Calcd. for $C_{15}H_{13}O_2N$: C, 78.53; H, 4.76; N, 5.01%.

The mother liquor was evaporated to remove most of the acetic acid and acetic anhydride, the orange residue dissolved in a mixture of benzene and petroleum benzine and submitted to column chromatography by the use of activated alumina (10 g.). Only a small amount of dark resinous substance remained on the column and further chromatographic separation of the effluent afforded two sorts of crystalline compound.

1) Colorless small plates melting at 129~130°C gave 4, 2', 4'-trinitroterphenyl and thus was identified as 2'-nitroterphenyl. Yield ca. 20%.

Found: N, 5.03, 5.15. Calcd. for $C_{15}H_{13}O_2N$: N, 5.01%.

2) Clear yellow plates melting at 126~127°C were identified as 2-nitroterphenyl. The corresponding amine, and acetylated amine gave the same melting points with those in the literature. Yield, 15 to 20%.

Found: N, 5.00, 5.12. Calcd. for $C_{15}H_{13}O_2N$: N, 5.01%.

Reduction of 4-Nitroterphenyl.—II (250 g.) in hot isoamyl acetate (8 l.) was gradually added to a warm mixture of ethanol (8 l.) and 11 N hydrochloric acid (2 l.) containing stannous chloride (dihydrate, 2 kg.) with a good stirring. The mixture was boiled for 30 min.; the almost colorless 4-aminoterphenyl hydrochloride (III) was filtered off, washed with ethanol, suspended in 0.1 N hydrochloric acid, boiled to remove ethanol and filtered off. The reduction was almost quantitative.

Diazotization and the Sandmeyer Decomposition.—To a freshly prepared suspension of III in water (20 l.) containing 11 N hydrochloric acid (250 ml.) and zinc chloride (dihydrate 50 g.), was dripped sodium nitrite (80 g.) in water (1 l.) with good stirring. This was continued for 3 hr. after the addition of nitrite, the temperature being kept at 10°C. No apparent change was observed. The excess of nitrite having been decomposed with urea, the suspension was treated with potassium iodide (200 g.) solution and heated to nearly boiling. When the suspension became colorless and the evolution of nitrogen ceased, the precipitate was filtered off, washed with sodium sulfite solution and dried. Powder of crude 4-iodoterphenyl (IV) was dissolved in hot xylene filtered and shaken first with hot 6 N sodium hydroxide solution and then with hot 6 N sulfuric acid containing stannous chloride and filtered. The filtrate was evaporated to remove most of the xylene and treated with ethanol to give pure IV, which was further distilled in vacuo (240°C, 10^{-2} mmHg) and recrystallized from isoamyl acetate. Yield, 40% based on II, m.p. 247~248°C.

Found: C, 60.74, 60.60; H, 3.67, 3.62; I, 35.64, 35.60. Calcd. for $C_{15}H_{13}I$: C, 60.69; H, 3.68; I, 35.63%.

The Ullmann Condensation.—In a small test tube, the powder of IV was mixed with copper (1 to 4 by weight), freshly prepared from copper sulfate and zinc dust and dried in vacuo, and placed in a potassium hydrogen sulfate bath at 280°C for 15 min. The reaction mixture was extracted with xylene and the residue sublimed in vacuo (400°C, 10^{-3} mmHg) to give crude sexiphenyl (V). The yield of this crude product was 0.25 g. from 1 g. of IV, corresponding to 10% based on I.

Purification of Sexiphenyl.—The crude V (12 g.) was boiled in potassium cyanide solution (10%, 500 ml.) for 30 min., sublimed in vacuo and further purified by recrystallization or by zone refining.

Recrystallization.—Since V is very sparingly soluble in organic solvents, only those with high boiling points are useful. Tetralin and dibutyl phthalate were passed through a column (diameter, 25 mm.; length, 600 mm.) of activated alumina, distilled in vacuo and used for recrystallization in a nitrogen atmosphere. Sublimed V (0.1 g.) was dissolved in boiling tetralin (1 l.), filtered, and the filtrate gradually cooled to give fluorescent platelets, which were filtered off, washed with ethanol, and dried. The product melted to a translucent fluid at 420°C.

Found: C, 94.04, 93.96; H, 5.75, 5.74. Calcd. for $C_{36}H_{26}$: C, 94.29; H, 5.71%.

Zone Refining.—A Bridgemann type furnace (diameter, 35 mm.) was set up to give a narrow region (ca. 2 cm.) of the maximum temperature (450°C) and have a suitable temperature gradient. A Telex tube containing V in vacuo (10^{-4} mmHg) was caused to move downward at a rate of 3 cm. per hr. in the furnace. After this process a pale yellow mass with many dark brown stripes was obtained with a brown segregate on the top. The solid was taken out of the tube, the separable colored part removed and the yellowish mass was sublimed in vacuo. Almost colorless V came out, preceded by a small amount of yellowish substance, and a small amount of dark yellow residue remained. The sublimate consisted of almost pure V.

Since organic iodine compounds quench the fluorescence of organic scintillators to a marked extent[7], the removal of iodine was studied by repeated zone refining and vacuum sublimation. The sublimed V was submitted to zone refining and the iodine content of the solid determined by neutron activation analysis at various locations. The solid was then sublimed in vacuo and a similar cycle repeated. The results are summarized in Table II. It is seen that the difference in iodine content at varying locations in one lot is not marked but there appears to be an overall trend toward a lower iodine content with repetition of the cycle.

Examination of the Purity of Sexiphenyl.—The purity of V was examined by the usual chemical analysis and the neutron activation analysis.

Neutron Activation Analysis.—This is suitable for the determination of more than 0.005 μg. of iodine.

7) W. H. Helhuish and W. S. Metcalf, *J. Chem. Soc.*, 1958, 480.

The sample (10 mg.) was sealed in a polyethylene envelope and irradiated with thermal neutrons in a water-boiler type reactor for 1 hr. under a neutron flux 6×10^{11} neutrons per cm^2 per sec., together with a standard potassium iodide. The irradiated sample was swiftly taken out of the reactor and the counting rate due to iodine-128 (half life, 25 min.) was determined with a G. M. counter. A known portion of the standard was converted into silver iodide together with a known amount of carrier iodine and the counting rate similarly measured under the same condition. The radioisotope was identified by the measurement of the half life; carbon, hydrogen, oxygen and nitrogen give no appreciable amount of radioisotope.

A similar method was also useful for the determination of copper (more than 0.02 μg.) by the use of copper acetate as a standard. The irradiated sample was set aside until radioactive iodine decayed and submitted to scintillation spectrometry for the counting rate due to 0.51 MeV annihilation peak of copper-64 (half life, 12.8 hr.) to be measured. No appreciable amount of copper was found in sublimed V.

Measurement of the Melting Point.—This involved some experimental difficulty, because V melts at a very high temperature and sublimes to a significant extent at more than 350°C. The sample was sealed in a glass capillary in vacuo and placed in a quartz tube together with an Almel-Chromel thermocouple. The tube was heated from outside with nichrom wire and the temperature was read on a calibrated millivoltmeter. A fused sodium nitrate bath was also useful for the same purpose.

Summary

1) Mononitration of *p*-terphenyl is satisfactorily effected at 100 to 110°C in glacial acetic acid containing about 10% acetic anhydride and a trace of sulfuric acid, and 4-nitro- (ca. 60%), 2'-nitro- (20 to 25%) and 2-nitroterphenyl (15 to 20%) are obtained.

2) Sexiphenyl is formed in a fairly good yield (more than 40%) by the Ullmann condensation of 4-iodoterphenyl and copper.

3) Sexiphenyl is satisfactorily purified by repeated zone refining and vacuum sublimation. The final product melts at 428~429°C to form an apparent liquid crystalline state and becomes tranparent at 543°C (475°C in literature). It contains an appreciable amount of neither iodine nor copper and can be converted into a fairly large single crystal to be used as scintillator.

A part of the expenses was defrayed by a grant from the Ministry of Education, to which the authors' thanks are due.

Institute for Nuclear Study
The University of Tokyo
Tanashi, Tokyo
(M. T. and K. S.)

The Electrical Communication Laboratory, Musashino, Tokyo
(T. N.)

On the Reactivity of 4-Hydroxycyclohexyl p-Tosylates

By Nobuo MORI

(Received March 3, 1960)

The effect of a conformation on the reactivity in cyclohexane systems is very important*, and especially the difference in reactivity between *cis*- and *trans*-cyclohexane compounds serves generally for the study on their configurations.

The present paper describes the unexpected result that *trans*-4-hydroxy or -4-acetoxycyclohexyl *p*-tosylate was solvolyzed more rapidly than the corresponding cis isomer.

Results and Discussion

The solvolysis rates of 4-hydroxycyclohexyl *p*-tosylates were measured at 99.8°C in ethanol (98.5% by weight), and that of 4-acetoxycyclohexyl *p*-tosylates measured in acetic acid containing a slight excess of acetic anhydride. In all cases, except alkaline ethanolysis, the observed rates were of the first order and the error of the measurements was always lower than 3%. Since the mean rate constants of the acetolysis of the *cis*- and *trans*-4-acetoxylcyclohexyl *p*-tosylates were not substantially affected by addition of a small quantity of anhydrous sodium acetate, the acetolysis is probably of the unimolecular type. On the other hand, a calculated first order rate constant decreased gradually during the solvolysis of the isomeric hydroxycyclohexyl *p*-tosylates in ethanol containing sodium ethoxide in 0.02 mol./l., in agreement with the behavior of 3-methyl

* The importance was first pointed out by D. H. R. Barton (*Experientia*, **6**, 316 (1950)).

cyclohexyl *p*-tosylate described previously[1], and the mean rate constants were about 3 times of that in neutral ethanol. This fact suggests that a part of the alkaline ethanolysis consists of a bimolecular reaction based on the back-side attack of the ethoxide ion. Table I lists the data for a run with *cis*-4-acetoxycyclohexyl *p*-tosylate in acetic acid containing sodium acetate in 0.029 mol./l., while a run with *cis*-4-hydroxycyclohexyl *p*-tosylate in ethanol containing sodium ethoxide in 0.02 mol./l. is given in Table II. It is seen that in the former run a first order rate constant is satisfactorily constant and in the latter run a rate constant decreases gradually during the solvolysis.

Table I. Acetolysis of *cis*-4-acetoxycyclohexyl *p*-tosylate in acetic acid containing AcONa in 0.029 mol./l. at 99.8°C

Time, min.	Tosylate, mol./l.	$k_1\times10^5$, min^{-1}
0.0	0.0282	
30	0.0250	4.07
60	0.0220	4.14
90	0.0192	4.25
120	0.0173	4.03
150	0.0150	4.19
210	0.0122	4.03
	Mean	4.12

Table II. Ethanolysis of *cis*-4-hydroxycyclohexyl *p*-tosylate in ethanol containing EtONa in 0.02 mol./l. at 99.8°C

Time, min.	Tosylate, mol./l.	$k_1\times10^5$, min^{-1}
0.0	0.0180	
20	0.0094_5	3.68
30	0.0072	3.24
40	0.0058	3.01
50	0.0050	2.76
80	0.0031	2.30
	Mean	3.0

The rate constants and the relative rates for the isomeric tosylates are summarized in Tables III and IV, respectively.

Table III. Rate constants of solvolysis of 4-substituted cyclohexyl *p*-tosylates at 99.8°C

4-Substituent	Tosylate mol./l.	Solvent	Alkali mol./l.		$k_1\times10^5$ min^{-1}
cis-OH	0.018	a	0.020	c	3.0
	0.020	a			0.835
trans-OH	0.018	a	0.020	c	10
	0.020	a			2.97
cis-OAc	0.0282	b	0.0290	d	0.412
	0.0284	b			0.400
trans-OAc	0.0283	b	0.0292	d	1.10
	0.0284	b			1.00

a, ethanol; b, acetic acid; c, sodium ethoxide; d, sodium acetate.

Table IV. Relative rates of solvolysis of 4-substituted cyclohexyl *p*-tosylates

	4-OH		4-OAc	
Solvent	a	containing c	a	b containing d b
k_{trans}/k_{cis}	3.3	3.5	2.6	2.5

Generally, in solvolysis of rigid cyclohexane systems for example *t*-butylcyclohexyl *p*-tosylate, the compound where the departing group is axial is solvolyzed in ethanol, acetic acid or formic acid at a rate 3~4 times as fast as that of the corresponding isomer where the departing group is equatorial, and also in a mobile substituted cyclohexane system, as that shown in Fig. 1, where that two possible chair conformations are readily interconvertible, for example as 3-methoxycarbonylcyclohexyl *p*-tosylate[3] or 1, 3-di-*p*-toluenesulfoxycyclohexane[1], the solvolysis leads to an essencially similar result.

The possible conformations of 4-substituted cyclohexyl *p*-tosylates are as follows:

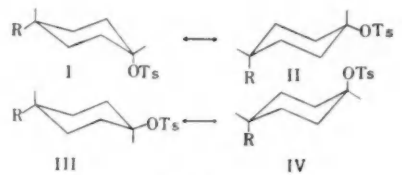


Fig. 1

where R is a substituent and Ts is the tosyl group. The conformation III of the trans form is probably more stable than the conformation IV, while the difference in stability between the conformation I and II of the cis form is probably very small or negligible, when R is not so large a group as *t*-butyl group. Thus, it is expected that the cis form is more reactive than the trans form, as described above.

However, in the present work, the *trans*-4-hydroxycyclohexyl *p*-tosylate was ethanolyzed at a rate 3.5 times as fast as that of the corresponding cis isomer, and also the *trans*-4-acetoxycyclohexyl *p*-tosylate was acetolyzed at a rate 2.5 times as fast as that of the corresponding cis isomer. These facts can not be explained on the basis of the general rule described above.

Further, the configuration of the isomeric cyclohexane-1, 4-diols, which was first established by Bayer[4], is in agreement with the chemical fact that, by direct dehydration of

1) N. Mori, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 1458 (1959).
2) S. Winstein and H. J. Holmess, *J. Am. Chem. Soc.*, **77**, 5562 (1955).
3) D. S. Noyce and H. J. Weingarten, ibid., **79**, 3103 (1957).
4) A. Bayer, *Ann.*, **278**, 92 (1894).

diol over alumina, the yield of 1,4-epoxycyclohexane from the *trans*-diol was much higher than that from the *cis*-diol[5], and it is probably right.

A further study concerning this problem will be reported shortly.

Experimental

Samples*: *cis*- and *trans*-Cyclohexane-1,4-diol.—Quinol (25 g.) in methanol (30 cc.) in an autoclave was hydrogenated at 120°C under 80 initial atm. in the presence of Raney nickel (10 g.) for about 3 hr. until no more hydrogen was absorbed. The filtered solution was evaporated under reduced pressure and the residue was acetylated by refluxing with acetic anhydride (70 cc.) for 3 hr. and the crude diacetate crystallized from hot acetone (30 cc.), to give prisms of the *trans*-diacetate which melted at 100.5~102°C after one recrystallization from ligroin (b. p. 75~120°C). The yield was 13.5 g. The acetone filtrate was concentrated, diluted with benzene (5 cc.) and then ligroin, and seeded with the *trans*-diacetate in a refrigerator, to give a small amount of this material. The residual solution was concentrated and placed with occasional stirring in a refrigerator for several days until it crystallized, to give the *cis*-diacetate which melted at 34~35°C after recrystallization from a small volume of ligroin. The yield was 12 g.

A solution of the *trans*-diacetate in absolute methanol (30 cc.) treated with a very small piece of metal sodium was refluxed for 30~60 min., concentrated to a small volume under reduced pressure, dissolved in hot dry ether and cooled to 0°C, to give as prisms the *trans*-diol, m. p. 144°C.

The *cis*-diacetate was similarly treated and the residue obtained by concentration of the reaction mixture was crystallized from hot acetone, to give as needles the *cis*-diol, m. p. 110°C.

The *trans*-diol (4.9 g.) in dry pyridine (25 cc.) was treated under stirring and cooling to 0~5°C with *p*-toluenesulfonyl chloride (7.52 g.) in chloroform (25 cc.). After stirring for 3 hr. at room temperature, the mixture was poured into excess of dilute hydrochloric acid cooled with ice, the resulting chloroform solution was washed with dilute hydrochloric acid, water and then a 10% solution of sodium carbonate, dried over sodium sulfate and evaporated under reduced pressure. The residue was dissolved in hot benzene, treated with hot ligroin and cooled to room temperature, to give the *trans*-monotosylate in needles, m. p. 112.5°C after recrystallization from benzene-ligroin.

When the reaction mixture, treated with *p*-toluenesulfonyl chloride as described above, was further treated with one equivalent quantity of acetyl chloride in chloroform, it gave the *trans*-acetoxy cyclohexyl *p*-tosylate in needles, m. p. 81~81.5°C after crystallization from benzene-ligroin.

When the *cis*-diol was similarly treated and recrystallized, the *cis*-hydroxycyclohexyl tosylate (m.p. 94~95°C) and the *cis*-acetoxycyclohexyl tosylate (m. p. 105°C) were obtained.

Solvents.—*Ethanol* (98.5% by weight).—Reagent grade absolute ethanol was fractionally distilled.

Acetic Acid.—Reagent grade glacial acetic acid was crystallized twice by the freezing method, refluxed with 2% by weight of acetic anhydride and 1% by weight of anhydrous sodium acetate for 3 hr. and distilled.

Procedure.—Rates were measured by the usual ampoule technique[7]. Concentrations are given at room temperature and the reaction was followed by the titration at intervals for the sulfonic acid liberated or the base consumed during the solvolysis. Titrations in acetic acid were carried out with a 0.05 N solution of AcONa or *p*-toluenesulfonic acid in acetic acid with bromophenol blue as indicator, and in ethanol a 0.05 N solution of sodium hydroxide or hydrochloric acid in water was used for titration with phenolphthalein as indicator. Rate constants were calculated from the formula

$$k_1 = 1/t \ln a/(a-x)$$

in which a was the initial concentration of tosylate and x was the concentration of sulfonic acid liberated or base consumed at time t.

The author expresses his sincere thanks to Professor Y. Tsuzuki for his advice during the investigation.

Department of Chemistry
Tokyo College of Science
Shinjuku-ku, Tokyo

5) R. C. Olberg, H. Pines and U. N. Ipatieff, *J. Am. Chem. Soc.*, **66**, 1096 (1944).

* All samples were prepared by the methods described in Ref. 6 with some modifications.

6) L. N. Owen and P. A. Robins, *J. Chem. Soc.*, **1959** 320.

7) N. Mori, This Bulletin, **33**, 1144 (1960).

Ultraviolet Absorption Spectra of Substituted Phenylureas. Part II[1]. *Solvent Effect and Structure of Carbamide Group*

By Yojiro Tsuzuki, Shinichi Motoki and Ritsuko Tanese

(Received April 11, 1960)

In the previous paper dealing with the ultraviolet absorption spectra of substituted phenylureas it was suggested that the carbamide group $-NHCONH_2$ behaves electronically as a peculiar substituent[1].

With disubstituted benzenes in general Doub and Vandenbelt found some semiquantitative relationships[2], which exist between the absorption displacement $\Delta\lambda$ and the electronic properties of the two substituents. Applying these empirical rules to the previous results, it has now been confirmed that the substituent $-NHCONH_2$ behaves as an electron-attracting or releasing group according as the other substituent is electron-releasing or attracting. During the course of an investigation of the unusual property of this group, attention has been drawn to the data given by Schroeder[3] of the spectra of ethyl phenylureas.

As is shown in Table I, *N*-ethyl phenylureas show markedly decreased intensity of absorption, whereas *N'*-ethyl derivatives exhibit strong

Table I. Ultraviolet absorption spectra of ethyl phenylureas (in ethanol)

	$\lambda_{1\,max}$	$\varepsilon_{1\,max}$	$\lambda_{2\,max}$	$\varepsilon_{2\,max}$
$C_6H_5NHCON'H_2$	237	17,700	268～275	1,100
$C_6H_5NC_2H_5CON'H_2$	235～237	3,480	no absorption	
$C_6H_5NC_2H_5CON'HC_2H_5$	243	3,630	no absorption	
$C_6H_5NHCON'HC_2H_5$	240～241	19,800	275～277	1,000
$C_6H_5NHCON'(C_2H_5)_2$	239～241	18,300	270～273	1,100

Table II. Absorption spectra of para-substituted phenylureas in aqueous, alcoholic and ethereal solution

Compounds	Absorption bands	Solvent		
		Water	Ethanol	Ether
$C_6H_5NHCONH_2$	λ_1	234	287	237.5
	ε_1	6,420	18,800	19,000
	λ_2	no absorption	274	275
	ε_2	〃	1,200	1,160
p-$C_2H_5OC_6H_4NHCONH_2$	λ_1	236.5	242	243.5
	ε_1	12,800	18,200	19,300
	λ_2	280	290	293.5
	ε_2	1,860	1,980	2,180
p-$CH_3C_6H_4NHCONH_2$	λ_1	236	240	241.5
	ε_1	12,400	18,400	20,100
	λ_2	272～276	281	281
	ε_2	650	1,090	1,290
p-$NO_2C_6H_4NHCONH_2$	λ_1	325～329	322	321.5
	ε_1	10,700	13,200	14,500
	λ_2	no absorpt.	no absorpt.	no absorpt.
	ε_2	〃	〃	〃
p-$CH_3OC_6H_4NHCONH_2$	λ_1	235	237	242
	ε_1	12,900	17,700	18,200
	λ_2	279	284.5	293.5
	ε_2	1,990	1,870	2,700

1) Part I. Y. Tsuzuki, S. Motoki and K. Migita, This Bulletin, **32**, 1189 (1959).

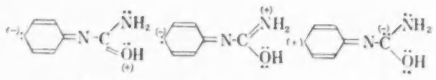
2) L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **69**, 2714 (1947).

3) W. A. Schroeder, *Anal. Chem.*, **23**, 1740 (1951).

absorption, as is observable in phenylurea itself. Since this effect of the alkyl group is likely to be observed in general when prototropy is set up in the systems[4], the following tautomerism (I, II, and III form) may be possible, and hence aryl ureas may, at least partly, be present in the pseudo form II. This form is impossible for *N*-alkyl phenylureas, which exhibit less intense absorptions.

$$\underset{\text{(I)}}{\text{ArNH–C(=O)–NH}_2} \quad \underset{\text{(II)}}{\text{ArN=C(–OH)–NH}_2} \quad \text{or} \quad \underset{\text{(III)}}{\text{ArNH–C(–OH)=NH}}$$

The electronically amphoteric property of the carbamide group is thus clearly shown with the following resonance structures of the isomer.



(IV) (V) (VI)

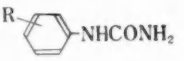
The presence of an acidic, enolizable hydrogen atom in the carbamide group is also supported by the fact that phenylureas are more soluble in aqueous alkalis than in water. From these considerations it becomes a theme of some interest to study the solvent effect on the spectra of these compounds for the purpose of getting further information on the nature of the group. In the present study were used some solvents of different polarity, such as water, ethanol and ethyl ether.

Results and Discussions

The experimental results are given in Tables II and III. It is clearly seen that the absorption intensity of the compounds increases markedly, as the polarity of the solvent decreases.

Now the remarkable solvent effect seen in Tables II and III should be considered. With common substances the extinction coefficient is, however, only slightly (5~7%) affected by the solvent, whereas the above cases are entirely different, namely ε_1 and ε_2 radically change on the whole according to the solvent. These remarkable solvent effects are occasionally observed by dissolving substances in such solvents as bring about some very mild chemical changes, as complex formation or displacement of tautomeric equilibrium[5]. Thus the data of the absorption spectrum are reasonably interpreted by assuming that in less polar solvents the equilibrium of tautomerism of aryl ureas moves towards the acidic pseudo form II which absorbs more intensely than the normal form I.

Table III. Absorption spectra in solution of ethoxyl and methoxyl phenylureas



Absorption	Solvent: Water	Ethanol	Ether
(a) R = *p*-C_2H_5O			
λ_1	236.5	242	243.5
ε_1	12,800	18,200	19,300
λ_2	279	290	293.5
ε_2	1,860	1,980	2,180
(b) R = *m*-C_2H_5O			
λ_1	238	240.5	242
ε_1	10,400	13,500	14,800
λ_2	278	280	280
ε_2	2,360	2,550	3,000
(c) R = *o*-C_2H_5O			
λ_1	236	241	242
ε_1	8,820	15,400	16,300
λ_2	278	281	281
ε_2	2,860	3,830	3,600
(d) R = *p*-CH_3O			
λ_1	235	237	242
ε_1	12,900	17,700	18,200
λ_2	279	284.5	293.5
ε_2	1,990	1,870	2,700
(e) R = *m*-CH_3O			
λ_1	238	236	241.5
ε_1	11,600	13,700	16,500
λ_2	277.5	275	280
ε_2	3,280	2,570	2,800
(f) R = *o*-CH_3O			
λ_1	237	236	241.5
ε_1	8,810	15,500	16,500
λ_2	277.5	275.5	281
ε_2	3,210	4,050	3,900

Another outstanding feature noticeable in Tables II and III is the blue shift of the absorption bands which shift further as the polarity of the solvent increases, however, with a few exceptions of *p*-nitro-, *m*-methoxy- and *o*-methoxy-phenylureas. This feature is peculiar, for increasing polarity of the solvent usually causes on the contrary a red shift of the absorption band[6].

To see clearly the effect of orientation (*o*, *m* and *p*-RO) on the red shift in ethoxy- and methoxy-phenylureas, the data in Table III were analyzed and the results are shown in Table IV.

4) See A. E. Gillam and E. S. Stern, "Introduction to Electronic Absorption Spectroscopy in Organic Chemistry", 2nd Ed., Edward Arnold Publishers, London (1957), p. 259.

5) A. E. Gillam and E. S. Stern, loc. cit., pp. 301–2. Cf. L. N. Ferguson, *Chem. Revs.*, **43**, 394 (1948).

6) A. E. Gillam and E. S. Stern, loc. cit., p. 303.

TABLE IV. ORIENTATION EFFECT ON BATHOCHROMIC SHIFT IN ETHOXYL AND METHOXYL PHENYLUREAS (ANALYSIS OF THE ABSORPTION DATA IN TABLE III)

Solvent	Compound	Relation	
		K-band	B-band
Ether	$C_2H_5OC_6H_4NHCONH_2$	$p>o=m$	$p\gg o>m$
Ether	$CH_3OC_6H_4NHCONH_2$	$p>o=m$	$p\gg o>m$
Ethanol	$C_2H_5OC_6H_4NHCONH_2$	$p>o>m$	$p\gg o>m$
Ethanol	$CH_3OC_6H_4NHCONH_2$	$p>o=m$	$p\gg o>m$
Water	$C_2H_5OC_6H_4NHCONH_2$	$m>p>o$	$p>o=m$
Water	$CH_3OC_6H_4NHCONH_2$	$m>o>p$	$p>o=m$

From Tables III and IV is noticed a third interesting phenomenon, namely, for B-band the absorption maximum of the alkoxy-phenylureas is in the order $p\gg o>m$ in both ethanol and ether, while in aqueous solution the three nuclear isomers absorb nearly the same wave length region; for the K-band, *m*-compounds absorb in aqueous solution the region of the longest wavelength ($m>p=o$), although the former relation $p>o>m$ nearly holds in ethanolic and ethereal solution.

These somewhat peculiar relations may be interpreted, at least partly, by the idea that in aqueous solution the carbamide group mainly takes the urea form, so that it loses the electron-attracting property as the result of the absence of resonance with the alkoxyl group, but in non-aqueous solutions the carbamide group assumes a greater part of the pseudo form, making the resonance possible with the alkoxyl group.

Thus the pseudo form of phenylureas is assumed and may be confirmed from various angles. For this purpose it is desirable to synthesize some of the pseudo derivatives, and to make a special study of the spectrum[7]. The result of this study will be reported in the next paper.

Experimental

Preparation of Compounds.—Substituted phenylureas were prepared from potassium cyanate and the corresponding nuclear substituted anilines by the methods described in "Organic Syntheses"[8]. *o*-Methoxyl phenylurea, m. p. 146.5°C, *m*-isomer, m. p. 130°C, *p*-isomer, m. p. 164~5°C. The solvents were purified by distillation. Ethanol was tested to be free from benzene.

Absorption Spectra.—The absorption spectra were measured in the region of 200~350 mμ by means of a Beckmann Model DU Quartz spectrophotometer with the solutions of concentration about 1/10,000 M.

Tokyo College of Science
Kagurazaka, Shinjuku-ku, Tokyo

7) See A. E. Gillam and E. S. Stern, loc. cit., p. 257.
8) F. Kurzer, "Organic Syntheses", Vol. 31, John Wiley & Sons, Inc. New York (1951), p. 8.

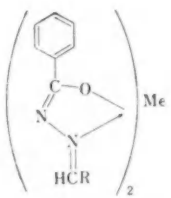
*Über die Kupfer(II)- und Nickel(II)-komplexsalze der Benzoylhydrazone einiger aliphatischen Carbonylverbindungen**

Von Hiroshi OHTA

(Eingegangen am 18. Februar, 1960)

Als Carbonylreagens bildet das Benzoylhydrazin mit den Aldehyden Benzoylhydrazone. Die Benzoylhydrazone der aromatischen Aldehyde sind in den organischen Lösungsmitteln ziemlich schwer löslich, diejenigen der aliphatischen Reihe sind aber spielend löslich. Im vorliegenden Experiment ist gezeigt worden, daß die ersteren mit zweiwertigem Kupfer- oder Nickel-Ion keine charakterisierbaren Komplexsalze geben, während die letzteren gut gebildete Komplexsalze liefern.

Zuerst sollen die Kupfer(II)- und Nickel-(II)-komplexsalze einiger aliphatischen Monoaldehyde beschrieben werden. Als Aldehydkomponente wurden Acetaldehyd (Äthanal), *n*-Butyraldehyd (*n*-Butanal), *n*-Önanthaldehyd



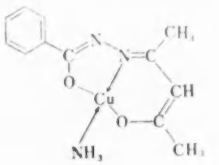
I

Me=Cu oder Ni.
R=1) CH_3, 2) $(CH_2)_2CH_3$, 3) $(CH_2)_5CH_3$, 4) $(CH_2)_9CH_3$.

* Organische Metallkomplexsalze IV. III. Mitteilung: H. Ohta, Dieses Bull., 33, 202 (1960).

(*n*-Heptanal) und *n*-Caprinaldehyd (*n*-Dekanal) ausgewählt. Die komplexsalze wurden aus dem Benzoylhydrazin, den Aldehyden und den Metallacetaten in Äthanol leicht dargestellt und in schönen Kristallen erhalten. Die Kupfersalze sind rötlich violett, die Nickelsalze gelbrot. Sie würden mit der Formel I formuliert werden können. Alle diese Komplexsalze, besonders diejenigen des *n*-Heptanal-benzoylhydrazons und des *n*-Dekanal-benzoylhydrozons sind in den meisten organischen Lösungsmitteln leicht löslich und die letzteren zwei zeigen ziemlich niedrige Schmelzpunkte kraft der längeren aliphatischen Ketten[1].

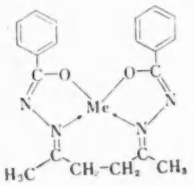
Dann werden die Kupfer(II)- und Nickel-(II)-komplexsalze der Benzoylhydrazone von den aliphatischen 1, 3- und 1, 4-Diketonen, dem Acetylaceton (2, 4-Pentandion) und dem Acetonylaceton (2, 5-Hexandion) beschrieben. Aus Benzoylhydrazin, 2, 4-Pentandion und Kupferacetat in alkoholischem Ammoniak wurde nur 2, 4-Pentandion-monobenzoylhydrazono-monoammin-kupfer(II) (Formel II), nicht 2, 4-Pentandion-dibenzoylhydrazono-kupfer(II) noch 1-Benzoyl-3, 5-dimethyl-pyrazol erhalten. Das entsprechende Nickelkomplexsalz konnte nicht erhalten werden, weil es so sehr leicht löslich war.



II

Die Komplexsalze vom 2, 3-Butandion-dibenzoylhydrazon waren schon von Sacconi[2] berichtet worden. Es ist klar, daß sie beständig sind, weil sie durch den Chelat- und Resonanzeffekt stabilisiert sind.

Um zu entscheiden, welche Komplexsalze das 2, 5-Hexandion-dibenzoylhydrazon gibt, welches zwei mehr Methylen-Gruppen enthält als 2, 3-Butandion-dibenzoylhydrazon, wurde die Synthese seiner Kupfer(II)- und Nickel(II)-komplexsalze versucht. Ein schwärzlich-braunes Kupfersalz und ein rotes Nickelsalz wurden erhalten, die nach den analytischen Daten mit der Formel III formuliert werden können, denn sie sind kristallinisch erhalten und in den organischen Lösungsmitteln leicht löslich.



III

Me=Cu oder Ni

Nach den Farben dieser Komplexsalze (Kupfersalze: rötlich-violett bzw. schwärzlich-braun, Nickelsalze: gelbrot bzw. rot) besitzen sie alle wohl quadratische, ebene Konfiguration. Die Struktur der Nickelkomplexsalze konnte sich aus der magnetischen Suszeptibilität erschließen**. Nach den magnetischen Messungen sind beide Bis-(Äthanal-benzoylhydrazono)-nickel(II) und 2, 5-Hexandion-dibenzoylhydrazono-nickel(II) diamagnetisch, was auf planen Bau hindeutet***.

Beschreibung der Versuche

Die magnetischen Messungen wurden mit der Gouyschen Waage ausgeführt.

Bis-(Äthanal-benzoylhydrazono)-kupfer(II). — Man gibt zur Lösung von 324 mg Äthanal-benzoylhydrazon[3] in 10 ccm Äthanol, 200 mg Kupferacetat (Monohydrat) in 5 ccm Wasser. Die Farbe der Lösung verändert sich zu Dunkelgrün und ein Niederschlag entsteht. Erwärmt man das Gemisch auf dem Wasserbade, so verwandelt sich der Niederschlag nach und nach in hell rötlich-violette Nadeln, die man aus 1, 4-Dioxan umkristallisiert. Hell rötlich-violette Nadeln.

Gef.: C, 56.08; H, 4.72; N, 14.57; Cu, 16.42. Ber. für $C_{15}H_{13}O_2N_4Cu$: C, 56.02; H, 4.70; N, 14.52; Cu, 16.46.

Bis-(Äthanal-benzoylhydrazono)-nickel(II). — Man gibt zur Lösung von 342 mg Äthanal-benzoylhydrazon in 10 ccm Äthanol, 250 mg Nickelacetat (Tetrahydrat) gelöst in 5 ccm Wasser. Es entsteht eine klare, dunkelblaue lösung, die sich durch kurzes Erwärmen auf dem Wasserbade in eine bräunlich-grüne verwandelt, aus der sich rötlich-gelbe Nadeln ausscheiden. Man kristallisiert sie aus dem Gemische von 1, 4-Dioxan und Äthylenglykol-monoäthyläther um. Rötlich-gelbe Nadeln.

Gef.: C, 56.70; H, 4.84; N, 14.70; Ni, 15.23. Ber. für $C_{15}H_{13}O_2N_4Ni$: C, 56.73; H, 4.76; N, 14.70; Ni, 15.41.

Bis-(n-Butanal-benzoylhydrazono)-kupfer(II). — Man gibt zur Lösung von 272 mg Benzoylhydrazin in 10 ccm Äthanol, 200 mg Kupferacetat (Monohydrat) in 5 ccm Wasser und darauf 144 mg *n*-Butanal. Es

1) Bezüglich der anderen Beispiele, siehe, T. Tsumaki und Mitarbb., *J. Chem. Soc. Japan Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 1086 (1957).

2) L. Sacconi, *Z. anorg. u. allgem. Chem.*, **275**, 249 (1954). *Chem. Abstr.*, **48**, 8105^{g} (1954).

** Verschieden von der Konfigurationen der Nickelkomplexsalze, kann diejenige der Kupferkomplexsalze allein nur aus der magnetischen Suszeptibilität nicht eindeutig entschieden werden, weil die Kupfer(II)komplexe unabhängig von allen, möglichen Konfigurationen immer ein ungepaartes Elektron besitzen.

*** Die Beispiele sind sehr viel; s. z. B., A. E. Martell & M. Calvin, „Chemistry of the Metal Chelate Compounds", Prentice-Hall, Inc., New York (1952), S. 279, 283.

3) R. Stollé und E. Münch, *J. prakt. Chem.*, [2] **70**, 400 (1904).

entsteht sofort unter Selbsterwärmung eine dunkelblaue Lösung, die sich nach einigen Minuten trübt. Erwärmt man die Lösung auf dem Wasserbade, so verschwindet die Trübung und eine dunkel grünlichblaue Lösung entsteht, aus der nach dem Erkalten (wenn nötig, durch Reiben der Gefäßwand mit dem Glasstab) graülich rotviolette Kristalle auskristallisieren, die man aus Äthanol umkristallisiert. Rötlich-violette Nadeln, die bei 173～174°C (unkorr.) unter Zersetzung schmelzen. Ziemlich löslich in warmem Äthanol.

Gef.: C, 59.71; H, 5.97; N, 12.54; Cu, 14.20. Ber. für $C_{22}H_{26}O_2N_4Cu$: C, 59.78; H, 5.93; N, 12.68; Cu, 14.37.

Bis-(n-Butanal-benzoylhydrazono)-nickel(II). — Man fügt zur Lösung von 272 mg Benzoylhydrazin in 10 ccm Äthanol, 250 mg Nickelacetat (Tetrahydrat) in 5 ccm Wasser und darauf 144 mg *n*-Butanal zu. Es entsteht sofort eine dunkelblaue Lösung, die sich durch Erwärmen auf dem Wasserbade in eine bräunlich-grüne verwandelt, aus der sich rötlich-gelbe Nadeln ausscheiden, welche man aus dem Gemische von 1,4-Dioxan und Äthylenglykol-monoäthyläther umkristallisiert. Rötlich-gelbe Nadeln, die bei 207～208°C (unkorr.) unter Zersetzung schmelzen.

Gef.: C, 60.65; H, 5.91; N, 12.98; Ni, 13.11. Ber. für $C_{22}H_{26}O_2N_4Ni$: C, 60.44; H, 5.99; N, 12.82; Ni, 13.43.

Bis-(n-Heptanal-benzoylhydrazono)-kupfer(II). — Man gibt zur Lösung von 272 mg Benzoylhydrazin in 2 ccm Äthanol, 200 mg Kupferacetat (Monohydrat) in 10 ccm Äthanol, und darauf 228 mg *n*-Heptanal. Es entsteht sofort eine schwärzlich-blaue Lösung, die eine kurze Weile auf dem Wasserbade erwärmt wird. Beim Erkalten scheiden sich hell rötlich-violette Kristalle aus (wenn nötig, muß man die Gefäßwand mit dem Glasstab reiben, oder die Lösung etwas konzentrieren), die man aus Äthanol umkristallisiert. Hell rötlich-violette, zarte Nadeln, welche bei 118～119°C (unkorr.) schmelzen. Ziemlich löslich in warmem Äthanol.

Gef.: C, 63.84; H, 7.26; N, 10.71; Cu, 12.44. Ber. für $C_{28}H_{38}O_2N_4Cu$: C, 63.91; H, 7.28; N, 10.65; Cu, 12.07.

Bis-(n-Heptanal-benzoylhydrazono)-nickel(II).—Man gibt zur Lösung von 272 mg Benzoylhydrazin in 10 ccm Äthanol, 250 mg Nickelacetat (Tetrahydrat) in 7 ccm Wasser und darauf 228 mg *n*-Heptanal. Es entsteht anfangs eine dunkelblaue, klare Lösung, die sich aber nach einigen Sekunden unter Trübung in eine schmutzig gelbgrüne verwandelt, aus der gelbrote Kristalle auszufallen beginnen. Nach der beinahe vollkommenen Ausscheidung der Kristalle, fügt man noch 3 ccm Wasser hinzu. Die Lösung trübt sich, welche aber durch Umrühren unter Abscheidung von noch einer kleinen Menge Kristalle klar wird. Man kristallisiert das Salz aus Äthylenglykol-monoäthyläther um. Gelbrote Blättchen, die bei 120～121.5°C (unkorr.) schmelzen.

Gef.: C, 64.56; H, 7.48; N, 10.58; Ni, 11.11. Ber. für $C_{28}H_{38}O_2N_4Ni$: C, 64.51; H, 7.35; N, 10.75; Ni, 11.26.

Bis-(n-Dekanal-benzoylhydrazono)-kupfer(II).—Man stellt es in derselben Weise wie beim Bis-(*n*-Heptanal-benzoylhydrazono)-kupfer(II) aus 272 mg Benzoylhydrazin in 2 ccm Äthanol, 200 mg Kupferacetat (Monohydrat) in 10 ccm Äthanol und 313 mg *n*-Dekanal dar und kristallisiert aus Äthanol um. Rötlich-violette, zarte Nadeln, die bei 106～107°C (unkorr.) schmelzen. Ziemlich löslich in warmem Äthanol.

Gef.: C, 66.98; H, 8.25; N, 9.24; Cu, 10.35. Ber. für $C_{34}H_{50}O_2N_4Cu$: C, 66.91; H, 8.26; N, 9.18; Cu, 10.41.

Bis-(n-Dekanal-benzoylhydrazono)-nickel(II).—Man fügt zur Lösung von 272 mg Benzoylhydrazin in 10 ccm Äthanol, 250 mg Nickelacetat (Tetrahydrat) in 5 ccm Wasser und darauf 313 mg *n*-Dekanal hinzu. Es entsteht sofort eine dunkelblaue, klare Lösung, die sich bald trübt; aus der getrübten Lösung scheiden sich schöne, gelbrote Kristalle aus, welche man aus 1,4-Dioxan umkristallisiert. Rötlich-gelbe Säulchen, die bei 108～109°C (unkorr.) schmelzen.

Gef.: C, 67.33; H, 8.23; N, 9.30; Ni, 9.55. Ber. für $C_{34}H_{50}O_2N_4Ni$: C, 67.44; H, 8.32; N, 9.25; Ni, 9.69.

2,4-Pentandion-monobenzoylhydrazono-monoammin-kupfer(II).—Man löst 272 mg Benzoylhydrazin in 200 mg 2,4-Pentandion durch Erwärmen, und darauf fügt man 5 ccm Äthanol zur Lösung zu. Gibt man zu dieser Lösung eine Lösung von 400 mg Kupferacetat (Monohydrat) in 10 ccm wässrigem Ammoniak (ca. 28%), so entsteht sofort eine schwärzlich-grüne, klare Lösung, die man auf dem Wasserbade so lange erwärmt, bis eine kleine Menge Kristalle auf der Oberfläche schwimmt. Beim Erkalten scheiden sich sehr langsam glänzende, schwärzlich-grüne Nadeln aus.

Gef.: C, 48.25; H, 5.19; N, 14.12; Cu, 21.11. Ber. für $C_{12}H_{12}O_2N_2 \cdot NH_3 \cdot Cu$: C, 48.56; H, 5.09; N, 14.16; Cu, 21.41.

2,5-Hexandion-dibenzoylhydrazono-kupfer(II). — Man gibt zur Lösung von 272 mg Benzoylhydrazin in 15 ccm Äthanol, 114 mg 2,5-Hxandion und darauf 200 mg Kupferacetat (Monohydrat) in 5 ccm Wasser. Es entsteht sofort eine dunkelgrüne Lösung, aus der sich beim kurzen Erwärmen glänzende, schwärzlich-braune Kristalle ausscheiden. Man kristallisiert sie aus 1,4-Dioxan um. Schwärzlich-braune, glänzende Rauten. Etwas löslich in Dioxan; Lösungsfarbe: dunkelgrün.

Gef.: C, 58.35; H, 4.97; N, 13.67; Cu, 15.41. Ber. für $C_{20}H_{20}O_2N_4Cu$: C, 58.31; H, 4.89; N, 13.60; Cu, 15.42.

2,5-Hexandion-dibenzoylhydrazono-nickel(II).—Man gibt zur Lösung von 272 mg Benzoylhydrazin in 20 ccm Äthanol, 114 mg 2,5-Hexandion und darauf 250 mg Nickelacetat (Tetrahydrat) in 5 ccm wässrigem Ammoniak (ca. 28%). Eine hellviolette Lösung entsteht, die sich durch Erwärmen auf dem Wasserbade in eine dunkelgrüne, dann in eine bräunlich-grüne verwandelt. Engt man diese Lösung auf dem Wasserbade stark ein, so scheiden sich rote Kristalle aus, die man aus 1,4-Dioxan umkristallisiert. Rote, glänzende Rauten.

Gef.: C, 59.10; H, 5.07; N, 13.84; Ni, 14.32. Ber. für $C_{20}H_{20}O_2N_4Ni$: C, 59.00; H, 4.95; N, 13.76; Ni, 14.42.

Zum Schluß möchte ich meinem Lehrer, Herrn Prof. Dr. Tokuichi Tsumaki für die Unterstützung und Forderung dieser Arbeit

meinen herzlichen Dank aussprechen. Herrn Professor Dr. Ryohei Matsuura und Herrn Dr. Yasushi Koga (Physikalisch-chemisches Laboratorium) für die magnetischen Messungen danke ich auch herzlichst. Herrn Michio Shido und Frl. Sachiko Indo (Laboratorium der Elementaranalyse, Kyushu Universität) verdanke ich die Durchführung der C-, H- und N-Bestimmungen.

Chemisches Institut
Naturwissenschaftliche Fakultät
Kyushu Universität
Hakozaki, Fukuoka

Determination of Oxygen in Some Minerals Using Pyrite

By Iwaji IWASAKI, Takashi KATSURA and Minoru YOSHIDA

(Received February 26, 1960)

A few years ago some experiments on the reactions among various kinds of sulfides, sulfates and oxides which occur in volcanic and hot spring districts were carried out by the present authors to ascertain the relations of their formation and occurrence[1]. The results of the experiments indicated that the amount of oxygen in some minerals can be easily determined with pyrite.

It has been pointed out that pyrite is easily oxidized during the process of grinding in the air and that a remarkable error may be introduced into the result of chemical analysis of pyrite from this oxidation[2]. While no method has yet been found to determine the minute amount of oxygen in pyrite, some reports described oxidation products of pyrite. From those reports, it would be concluded that iron sulfates may be formed by the oxidation[3,4]. In addition to these products, fine powder of pyrite may absorb moisture and oxygen from the air, and it should also be considered that the sample of pyrite may be contaminated with the small amount of oxides or sulfates contained originally in the raw minerals. Thus iron oxides, absorbed oxygen and absorbed water could be the sources of oxygen in pyrite samples, even if the samples, were almost pure under microscopic observation. And it should be pointed out that the oxygen in the samples reacts with the pyrite and is liberated as sulfur dioxide on heating the samples at a high temperature in vacuo. If the liberation of sulfur dioxide is quantitative, the amount of oxygen in the samples can be estimated from that of the sulfur dioxide evolved.

When moisture exists, hydrogen sulfide may also be formed, and the situation may be somewhat complicated because of the equilibrium among hydrogen sulfide, sulfur dioxide and water vapour. The nature of these reactions should be carefully investigated to establish an accurate method for the determination of oxygen in pyrite and other minerals. There are some reports on the reactions between pyrites and iron oxides[5], iron sulfates[6,7] and water[8], but the results are insufficient for the present purpose. In the present paper, the results obtained on these reactions and the method for the determination of a minute amount of oxygen in pyrite and the amount of oxygen in other minerals by using pyrite are given.

Experimental

Materials.—Natural pyrites used in the present study had a chemical composition* nearly equal to the ideal chemical formula, FeS_2, and the values obtained for the lattice constant of crystals agreed well with the data described by Parker and Whitehouse[9], and also by Hiemstra[10] (5.416～5.417Å). Iron monosulfide was obtained by thermal decomposition of the pyrites at about 900°C in vacuo. The chemical composition of the artifical

1) I. Iwasaki, T. Katsura and M. Yoshida, read before the 10th Annual Meeting of the Chemical Society of Japan, Tokyo, 1957.
2) E. A. Hontoir, *Bull. Inst. Mining. Met.*, No. **553**, 95 (1952).
3) A. Wurm, *Z. prakt. Geol.*, **35**, 130 (1927).
4) G. E. Mapstone, *Chemistry & Industry*, **1954**, 577.
5) F. Martin and O. Fuchs, *Z. anorg. Chem.*, **125**, 307 (1922).
6) Kothny, *Met.*, **8**, 392 (1911) (cited by Gmelin's Handbook).
7) Gorgew, *Compt. rend.*, **104**, 1174 (1887) (cited by Gmelin's Handbook).
8) E. Grünnert, *J. prakt. Chem.*, [2], **122**, 91 (1929).
* The accurate chemical composition of these pyrites will be reported in another paper.
9) H. M. Parker and W. J. Whitehouse, *Phil. Mag.*, **14**, 939 (1932).
10) S. A. Hiemstra, *Am. Mineralogist*, **41**, 519 (1956).

iron monosulfide was somewhat richer in sulfur, and its chemical formula was $FeS_{1.03}$. It was not ferromagnetic and its properties agreed well with those of troilite under microscopic observation. Magnetite was obtained by thermal decomposition of reagent grade α-ferric oxide in a quartz tube at about 1200°C and below 1×10^{-4} mmHg of oxygen pressure achieved by pumping it out. The magnetite obtained as above had almost the ideal chemical composition, 49.9% FeO and 50.1% Fe_2O_3 in molar ratio. Other chemicals, such as α-ferric oxide, ferrous sulfate $FeSO_4\cdot7H_2O$, and ferric sulfate $Fe_2(SO_4)_3\cdot nH_2O$ [78% $Fe_2(SO_4)_3$] employed were all of reagent grade. The reagents were used after removing the water by heating in vacuo.

Apparatus and Procedure. — The apparatus employed is shown in Fig. 1. The maximum temperature attained is about 1000°C.

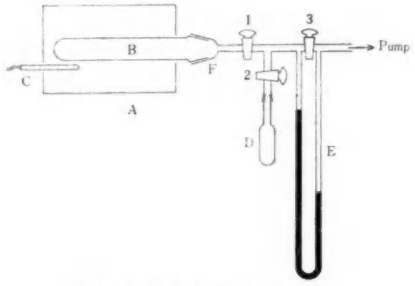


Fig. 1. Apparatus
A. Electric furnace
B. Quartz tube
C. Thermocouple
D. Absorption tube
E. Manometer
1,2,3 Cock

The finely powdered mixture of the sample with the pyrite was packed in a small quartz tube, and then placed at the bottom of a quartz combustion tube B (Fig. 1). Then all of the apparatus was evacuated to a pressure of $10^{-2}\sim10^{-3}$ mmHg. To analyse the gas evolved from the sample, potassium hydroxide was placed in tube D. After evacuation, cocks 2 and 3 were closed, then the temperature was raised at a rate of about 200°C per hr. The pressure of the evolved gas was continuously measured. The correction of the pressure for the temperature change was experimentally determined, and the volume of the evolved gas was calculated in N. T. P. When the reaction came to the end, cock 2 was opened, and the pressure of the unabsorbed gas was determined. This was usually very low in all of the present experiments. Potassium hydroxide which absorbed the acid gas was then dissolved in water and was poured into a suspension of freshly precipitated basic cadmium carbonate. By this procedure hydrogen sulfide is fixed in the precipitate as cadmium sulfide and sulfur dioxide remains in the filtrate as sulfite ions. The amount of hydrogen sulfide from the precipitate and the amount of sulfur dioxide from the filtrate were determined by iodometric titration. As the gas evolved from the reactions of the oxide and the sulfate with the pyrite contained only a negligible amount of hydrogen sulfide, the amount of sulfur dioxide could be determined directly by the manometric method. The nature of the solid products was also examined by chemical, X-ray and microscopic methods.

Results and Discussion

When the powdered pyrite alone was heated in the apparatus, a dissociated sulfur was deposited inside F the silica tube, and in some cases the evolution of a small amount of a gas which was stable at room temperature was observed. The analysis of the gas showed that it consists mainly of sulfur dioxide, hydrogen sulfide and water vapor, and that its amount is influenced to some extent by the degree of pulverization or other conditions. Therefore, a correction must be made for each kind of pyrite, when the volume of the sulfur dioxide evolved by the reaction between pyrites and iron oxides or iron sulfates is measured. From the repeated blank experiments, the blank values for the pyrite used in the present experiments were obtained as shown in Table I:

Table I

Temp. range	Correction ml. per 1 g. pyrite
Below 450°C	Almost negligible
450~550°C	2.5
550~650°C	3.0

(1) The Reaction between Pyrite and Ferric Oxide.—As will be seen in Fig. 2, the reaction between pyrite and ferric oxide begins at about 500°C and comes to the end at about 600°C. When an excess of pyrite exists, the solid product of the reaction is only troilite, and the reaction may be regarded as follows:

$$7FeS_2+2Fe_2O_3=11FeS+3SO_2 \qquad (1)$$

The amount of sulfur dioxide evolved from

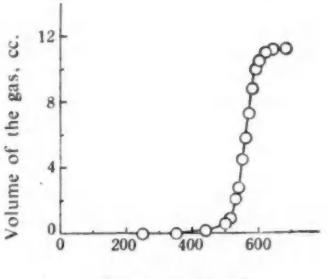


Fig. 2. Reaction between pyrite and α-ferric oxide (1).
Pyrite 200 mg.
Fe_2O_3 50 mg.

the mixture of 200 mg. of pyrite and 50 mg. of ferric oxide was 10 ml. (0°C, 1 atm.) in the range 500~600°C, and the value calculated from Eq. 1 is 10.5 ml.

When the amount of pyrite was insufficient to reduce all ferric oxide to troilite, the reaction was likely to proceed through two stages as shown in Fig. 3. The first stage of the reaction would correspond to Eq. 1, and the second to Eq. 2, which shows the reaction between the troilite and the remainder of the ferric oxide.

$$FeS + 10Fe_2O_3 = SO_2 + 7Fe_3O_4 \quad (2)$$

All the results such as the amount of gas evolved through each stage, the range of the reaction temperature, and the properties of the solid products observed by X-ray and microscopic method support the assumption described above. Martin and Fuchs[2] studied the reaction of similar mixtures of pyrite and

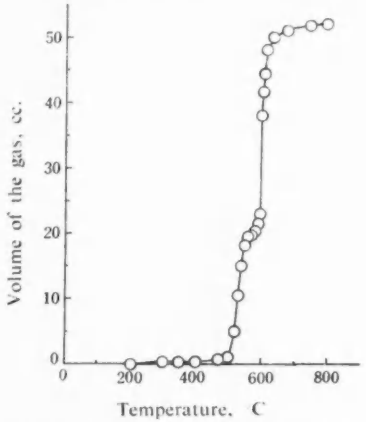


Fig. 3. Reaction between pyrite and α-ferric oxide (II).

Pyrite	250 mg.
Fe_2O_3	2.0 g.

ferric oxide (weight ratio 1 : 2.25 or 1 : 3) and obtained a mixture of troilite and magnetite as solid products. The co-existence of these solid phases can be interpreted by the results obtained by our experiments, but according to theirs, the reaction began at 570°C, came to the end at 870°C, and the range of the reaction temperature was higher than that obtained by the present authors.

As the ferric oxide reacts completely with the pyrite to liberate sulfur dioxide at about 600°C as shown in Fig. 2, the amount of the ferric oxide in the iron sulfides can be determined by measuring the amount of sulfur dioxide evolved from the samples with a sufficient amount of pyrite.

(2) The Reaction between Pyrite and Magnetite.—Magnetite (Fe_3O_4) also reacts with pyrite to form troilite and sulfur dioxide at a high temperature as shown in Eq. 3.

$$5FeS_2 + Fe_3O_4 = 8FeS + 2SO_2 \quad (3)$$

The amount of the gas evolved was in good agreement with Eq. 3. The reaction began at about 550°C, and came to the end at about 650°C as shown in Fig. 4. The temperature range of the reaction overlapped with that of the reaction between pyrite and ferric oxide. Magnetite did not react practically with troilite below 1000°C.

As magnetite reacts completely with the pyrite to liberate sulfur dioxide at about 650°C as shown in Fig. 4, the amount of the magnetite in the iron sulfides can be determined by measuring the amount of sulfur dioxide evolved from the samples with a sufficient amount of pyrite.

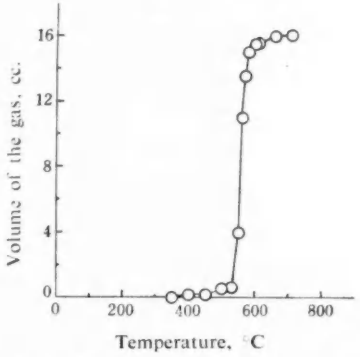


Fig. 4. Reaction between pyrite and magnetite.

Pyrite	200 mg.
Fe_3O_4	100 mg.

(3) The Reaction between Pyrite and Ferric Sulfate.—When sufficient amount of pyrite is present, the reaction between pyrite and ferric sulfate began at about 300°C and came to an end at about 650°C proceeding through three stages as shown in Fig. 5. The final product was only troilite, and the equation of the reaction in each stage can be considered as follows:

The first stage (about 300~420°C)

$$FeS_2 + 3Fe_2(SO_4)_3 = 7FeSO_4 + 4SO_2 \quad (4)$$

the second stage (about 450~520°C)

$$FeS_2 + 8FeSO_4 = 3Fe_3O_4 + 10SO_2 \quad (5)$$

the third stage (about 550~650°C)

$$5FeS_2 + Fe_3O_4 = 8FeS + 2SO_2 \quad (3)$$

The volumes of sulfur dioxide calculated from

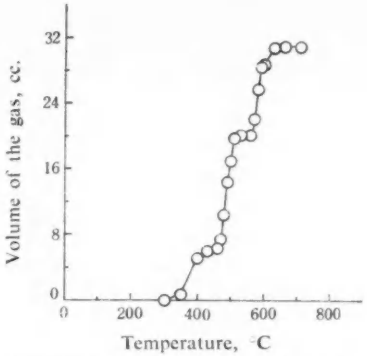


Fig. 5. Reaction between pyrite and ferric sulfate.

Pyrite	200 mg.
$Fe_2(SO_4)_3 \cdot nH_2O$	100 mg.

TABLE II

Example 1 $Fe_2(SO_4)_3 \cdot nH_2O$ 0.1 g., FeS_2 0.2 g.

	SO_2 found, ml.	SO_2 calcd., ml.
First stage	6.0	5.8
Second stage	13	12.7
Third stage	10	9.7

Example 2 $Fe_2(SO_4)_3 \cdot nH_2O$ 0.2 g., FeS_2 0.4 g.

	SO_2 found, ml.	SO_2 calcd., ml.
First stage	12	11.6
Second stage	26	25.4
Third stage	20	19.4

the Eqs. 4, 5 and 3 agreed fairly well with the experimental data for each stage as is seen in Table II. The range of the reaction temperature of the third stage agrees with that of the reaction described in section 2. To ascertain these equations, the reactions were cut off at the end of each stage by a rapid cooling and the solid products were examined. The product of the first stage was extracted by water, and the ferrous ion in the aqueous solution was titrated by a standard potassium permanganate solution. The value for ferrous sulfate in the solution was 56 mg. which agrees well with the value 54 mg. calculated by Eq. 4. The product of the second stage was strongly ferromagnetic with black color, and its X-ray diagram showed the diffraction lines of magnetite. These results showed that the reaction could be adequately expressed by Eqs. 4, 5 and 3. When the amount of pyrite was reduced, the product was changed as was expected from the Eqs. 3—5.

As ferric sulfate also reacts completely with pyrite to liberate sulfur dioxide around 650°C as shown in Fig. 5, the amount of ferric sulfate in the iron sulfides can be determined by measuring the amount of the sulfur dioxide liberated with a sufficient amount of pyrite.

(4) The Reaction between Pyrite and Ferrous Sulfate.—Remembering the three stages of the reaction between pyrite and ferric sulfate described above, the reaction between pyrite and ferrous sulfate would be considered to proceed similarly to the second and the third stage. As will be seen in Fig. 6, the reaction proceeds actually as was expected. Thus, the determination of ferrous sulfate in the mixture of ferrous sulfate and iron sulfides is possible from the amount of sulfur dioxide liberated when they are heated with a sufficient amount of pyrite at about 650°C in vacuo.

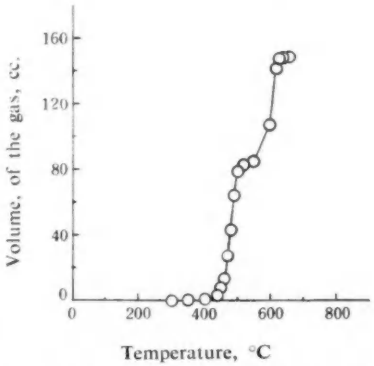


Fig. 6. Reaction between pyrite and ferrous sulfate.

Pyrite	1.0 g.
$FeSO_4 \cdot 7H_2O$	450 mg.

When the amount of pyrite was insufficient, hematite was formed as a final product.

$$FeS_2 + 11FeSO_4 = 6Fe_2O_3 + 13SO_2 \qquad (6)$$

When the amount of pyrite was less than that of the stoichiometric ratio of Eq. 6, sulfur trioxide and oxygen were also liberated by the decomposition of the remainder of the ferrous sulfate.

(5) The Determination of Ferric Sulfate, Ferrous Sulfate and Magnetite in their Mixture.—When a sufficient amount of pyrite is present, the reaction between ferric sulfate and pyrite proceeds through three stages as stated above. The second stage of the reaction corresponds to the reaction between pyrite and ferrous sulfate, and the third stage to the reaction between pyrite and magnetite. Consequently when a mixture of ferric sulfate, ferrous sulfate and magnetite is heated with a sufficient amount of pyrite, all the gas liberated at the first stage may be attributed to ferric sulfate, and that at the end of the second stage to ferric sulfate and ferrous sulfate, and that at

the end of the third stage to ferric sulfate, ferrous sulfate and magnetite. Therefore, the amount of each substance in the mixture can be determined from the amount of sulfur dioxide liberated at each stage of the reaction. Some results of these determinations of the amount of each substance by this procedure are shown in Table III. As will be seen in Table III, the accuracy of this procedure is sufficient for the present study.

Table III

	Example 1		Example 2	
	Added mg.	Found mg.	Added mg.	Found mg.
$Fe_2(SO_4)_3 \cdot nH_2O$	70	70	50	55
$FeSO_4 \cdot 7H_2O$	50	54	50	48
Fe_3O_4	30	33	50	54

(6) The Determination of a Very Small Amount of Oxygen in Pyrite. — The results of the experiments on the reactions between pyrite and iron oxides or sulfates show that the oxygen contained in iron oxides or sulfates are completely liberated as sulfur dioxide, when the samples are heated at 650°C in vacuo with a sufficient amount of pyrite. Therefore, when the powdered pyrite contains a small amount of oxygen-iron compounds such as Fe_2O_3 and $FeSO_4$, the total amount of oxygen in the pyrite sample can be determined by the present method. But, as already mentioned above, absorbed oxygen and absorbed water which can not be removed by pumping at a low temperature may be conceivable as another source of oxygen.

The absorbed oxygen will be evolved as sulfur dioxide at 650°C, because the vapor pressure of sulfur in equilibrium with pyrite is fairly high in this condition[11-13] and oxygen is readily converted into sulfur dioxide. Minden[14] reported that the evaporated film of lead sulfide chemisorbs oxygen and evolves it as sulfur dioxide above 200°C. His results may support the view that oxygen absorbed on the surface of pyrite is evolved as sulfur dioxide on heating.

On the reaction between pyrite and water at a high temperature, Grünnert[8] concluded that the reaction proceeds as follows:

$$\text{(I)} \quad 2FeS_2 = 2FeS + S_2$$

$$\text{(II)} \quad 3S_2 + 4H_2O = 4H_2S + 2SO_2$$

$$\text{(III)} \quad FeS + H_2O = FeO + H_2S$$

$$\text{(IV)} \quad 3FeO + H_2O = Fe_3O_4 + H_2$$

These equations may explain the results of his experiments using a large amount of water. However, the amount of water absorbed on the surface of pyrite may be too small to follow the reactions III and IV. Therefore, in our case the reaction between pyrite and water may proceed as the following Eq. 7.

$$3FeS_2 + 2H_2O = 3FeS + 2H_2S + SO_2 \qquad (7)$$

in which water vapor, sulfur dioxide and hydrogen sulfide are equilibrated with pyrite and troilite. From these facts, the amount of oxygen in pyrite can readily be determined by that of sulfur dioxide, hydrogen sulfide and water vapor.

When a small crystal of pyrite was heated without being pulverized, a small amount of gas was liberated and the pyrite was completely decomposed to troilite and sulfur. But, when the same sample was pulverized and heated, a larger amount of gas was liberated as will be seen in Fig. 7. From this fact, it is obvious that as a result of pulverization of pyrite, oxidation occurs or absorption of oxygen or water. The evolved gas was completely absorbed by potassium hydroxide, and about two thirds of the absorbed gas was sulfur dioxide and hydrogen sulfide, and the remainder seems to be water vapor as will be shown in the following experiments. Phosphorus pentoxide was placed in tube D in Fig. 1 and cock 2 was

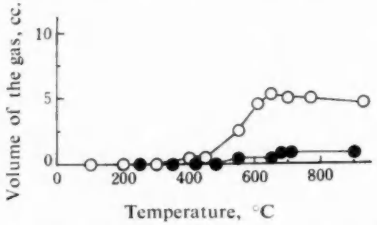


Fig. 7. Evolution of the gas from pyrite (1 g.)
● crystal ○ powder

Table IV

	Experiment 1	Experiment 2
Sample weight	3.0 g.	2.0 g.
Total volume of the gas evolved	3.0 ml.	1.7 ml.
SO_2	0.85 ml. (2.9 mg.)	0.70 ml. (2.0 mg.)
H_2S	0.98 ml. (1.5 mg.)	0.52 ml. (0.79 mg.)
H_2O	1.17 ml. (0.94 mg.)	0.48 ml. (0.39 mg.)
O attributed to SO_2	1.4 mg.	1.0 mg.
O attributed to H_2O	0.8 mg.	0.34 mg.
Total amount of O	2.2 mg.	1.34 mg.
O content	0.073%	0.067%

11) R. Juza and W. Biltz, *Z. anorg. allg. Chem.*, **205**, 273 (1932).
12) L. D'or, *J. Chim. Phys.*, **28**, 377 (1931).
13) G. M. Schwab and J. Philinis, *J. Am. Chem. Soc.*, **69**, 2588 (1947).
14) H. T. Minden, *J. Chem. Phys.*, **23**, 1948 (1955).

kept open through the experiment. The amount of gas evolved was fairly small and it consists of only sulfur dioxide.

The results of the experiments for the determination of oxygen content of powder pyrite are shown in Table IV. As will be seen in the analytical results, the precision is sufficient for the present study.

Summary

In the present paper a method for the determination of a very small amount of oxygen in an almost pure pyrite was proposed. From the results of the fundamental experiments on the reactions between the pyrite and the other minerals containing oxygen, it was ascertained that oxygen is completely liberated as sulfur dioxide and water vapor by heating in vacuo. The reproducibility of this method is fairly satisfactory, but there are no standard samples to examine the accuracy of this method. The results of the experiments indicate that this method could be used as a method for estimating the degree of oxidation of almost pure pyrites, for determining the amount of oxygen in some minerals, and in some cases for calculating the ratio of the oxygen containing compounds in their mixtures. Moreover, it seems possible to use this method for the determination of oxygen in a mixture of sulfides and oxides or sulfates of other metals than iron, and also oxygen in the metals. After the work reported herein had been almost completed, the authors were informed of the work, "The Sulfur Method of Oxygen Determination in Metals", of Babko et al.[15,16] who reported a somewhat similar study on the determination of oxygen in metals by using elementary sulfur instead of pyrite.

The authors are much indebted to Professor T. Watanabe and Mr. A. Sasaki, Department of Geology, The University of Tokyo for kindly supplying the samples of pyrite and for the microscopic study. We also express our hearty thanks to Dr. S. Akimoto, Geophysical Institute, the University of Tokyo, for his great help and valuable advice in X-ray study.

Laboratory of Analytical Chemistry and Geochemistry
Tokyo Institute of Technology
Ookayama Meguro-ku, Tokyo

15) A. K. Babko, K. E. Kleiner and L. V. Markova, *Zavodskaya Lab.*, **22**, 640 (1956); *Chem. Abstr.*, **50**, 15339 g (1956).
16) A. K. Babko, A. I. Volkava and O. F. Drako, *Zavodskaya Lab.*, **23**, 136 (1957); *Chem. Abstr.*, **51**, 17591 c (1957).

Vapor Pressure of Zinc in Tin-Zinc Binary Liquid Alloy

By Kichizo Niwa, Toshio Yokokawa and Harue Wada

(Received April 7, 1960)

For the development of the theory of metallic solution, systematic studies on thermodynamics of multi-component systems are required as well as those on electric and magnetic properties. Vapor pressure measurements directly provide the activity or the partial molar free energy of mixing of vaporizing components, though their temperature coefficients or heat terms are not so reliable as those determined by the calorimetric method. In the present work the applicability of Knudsen's effusion method was examined for the measurement of low vapor pressure of liquid alloy. This method is convenient for a measurement of this kind because small quantities of samples are enough to determine the vapor pressures. Also the concentration change of alloys with measuring time does not bring big error on account of low values of vapor pressure. In Knudsen's method, two conditions must be fulfilled. Firstly, vaporization velocity from alloy surface is so great that the vapor phase in the crucible may be maintained at equilibrium pressure. Secondly, diffusion through bulk phase of the alloy to surface is so rapid as to compensate for the decrease in the concentration of the vaporizing component. In relation to the above conditions, the effect of an oxide film and diffusivity in alloy phase as compared with the vaporization velocity must be taken into consideration. In order to make these points clear the vapor pressure of zinc in tin-zinc

liquid alloy was measured. Further, thermodynamic excess functions of this system were discussed.

Experimental

Experimental Method.—In the effusion method vapor pressure is calculated from effusion velocity by an equation

$$P=\sqrt{\frac{2\pi RT}{M}}\cdot\frac{1}{KA}\cdot\frac{G}{\tau}\left(1+\frac{KA}{\alpha B}\right) \qquad (1)$$

where A is the geometric area of the effusion orifice and KA is the effective area. K is the Clausing factor, a correction for the inevitable thickness of the orifice. α is the accomodation coefficient and B is the effective vaporization area in the crucible. $KA/\alpha B$ is a correction term for deviation of pressure in the crucible from saturation. G is the weight (in grams) of effused molecule within time interval τ (sec.). M is the molecular weight of the effusing molecule. Other symbols mean ordinary quantities. In the temperature interval of this experiment, vapor pressure of tin may be neglected and besides zinc vapor is taken as monatomic, so M in this case becomes the atomic weight of zinc. As K cannot be precisely determined by experiment, the effective area KA has been determined by combining the effusion velocity of solid zinc and its vapor pressure, presented by Barrow[1]. The correction term $KA/\alpha B$ is negligible compared with unity, provided that α is not very small. As will be shown later, this correction was proved not necessary.

Apparatus.—The apparatus, which had been previously used in the authors' laboratory[2], was modified in the reading of thermobalance. The latter is shown in Fig. 1. The beam A is of

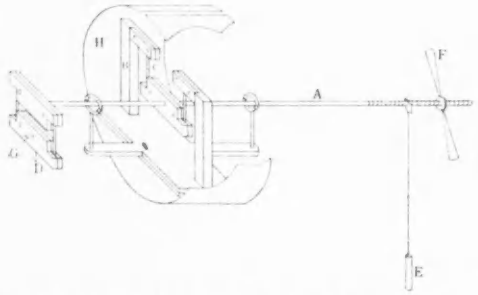


Fig. 1. Schematic diagram of the thermobalance.

aluminum and hung with a phosphorus bronze ribbon C from a frame of brass B, which is held in a brass vessel with a brass ring H. The effusion crucible is hung from D with a platinum wire. E is a dust core of 3 mm. in diameter and 1 cm. in length, and is used to convert the inclination of the balance into a change of electric current by means of a linear differential transformer. F is a counter weight of soft iron which can be shifted at a proper position along the beam by a magnet from the outside of the glass tube. A crucible of pyrex glass is 1 cm. in diameter and 1 cm. in height including its lid. An effusion orifice is bored at the center of the lid which is ground with the crucible. The orifice is ground as thin as possible (0.1 mm.) from both the up and down sides of the lid. The furnace consists of a porcelain tube wound by a nichrome resistance wire. The temperature was manually controlled at a constancy of ± 1°C during each measurement (20 min. to 2 hr.). Temperature was measured by a platinum vs. platinum-rhodium thermocouple, the end of which was nearly in contact with the crucible through a quartz tube. The thermocouple was calibrated at the melting points of zinc, tin, bismuth, lead and antimony.

Procedure.—About one gram of metal or alloy sample is placed in the crucible, which is hung from the thermobalance by a platinum wire of 0.2 mm. in diameter, then the counter weight is properly adjusted. Sensitivity of the balance is determined at each run by loading riders of known weight on G in Fig. 1 (about 0.1 mg./μA). Then a rider of the right weight is again loaded on the same position in order that the balance may be settled through the measuring time within the inclination range where the sensitivity has been measured. After that the system is evacuated to a pressure of 10^{-5} mmHg and the furnace is heated up to the desired temperature and the rate of weight loss is measured by way of the current in the transformer circuit.

Sample.—Purities of metals used are 99.9% (zinc), chemical pure (tin), 99.9% (bismuth), and 99.999% (indium). Zinc ribbon was used for the measurement in pure solid state. Alloys were prepared in the following way; pure metals of desired amount were sealed in a small pyrex tube in vacuo and kept at about 450°C for ten hr., followed by quenching.

Experimental Error.—As the sources of error of this measurement, temperature, area of the orifice, sensitivity of the balance and rate of change of current should be taken into account. Relative errors of these contents are 0.08, 2.7, 1.5 and 1% respectively. Then the fractional average deviation may amount to 3.2%. Next, the error of activity, calculated from the vapor pressure of pure liquid and alloys, amounts to 4%. The decrease in concentration of zinc with vaporization affects the activity coefficient by decreases of 6 and 3% at mole fractions of 0.05 and 0.1, respectively.

Measurement of Liquid Alloy.—The applicability of Knudsen's effusion method to alloy of liquid state was examined in the following points.

(A) Saturation of Vapor Phase.—In order to make certain that the vapor phase was saturated, vaporization velocity was measured, when the lid of the crucible was removed and the vapor freely escaped from the surface (nearly Langmuir-like). This velocity was about 1×10^{-2} mg./sec., while the ordinary effusion velocity was at most 6×10^{-4} mg./sec. Then, one can assume that zinc vapor is saturated in the crucible even in the case of liquid

1) R. F. Barrow et al., *Trans. Faraday Soc.*, **51**, 1354 (1955).
2) Z. Shibata and K. Niwa, *J. Fac. Sci. Hokkaido Imp. Univ.* Ser. III, Vol. II, 183 (1938).

solution, where a thin film of zinc oxide may cover and disturb vaporization, or may reduce the accommodation coefficient.

(B) Concentration Difference between the Surface and the Bulk Phase of Liquid Alloy.—The surface concentration of zinc decreases with its vaporization, while the concentration recovers by diffusion through the bulk phase. The following calculation has been made for the sake of estimation of this concentration gradient in the steady state. Assuming (a) that there exists a linear concentration gradient between the surface and a position, ΔL cm. distant under the surface, and (b) that there is no convection in the bulk phase, flow of zinc to the surface is given by

$$J(\text{g./sec.}) = -BD\Delta C/\Delta L$$

where B is the surface area and D, the diffusion coefficient of zinc in the solution and C, the concentration in g. per cc. This flow should be equal to effusion velocity at the steady state. The latter being at most 6×10^{-7} g./sec. at a vapor pressure of 10^{-2} mmHg, $\Delta C/\Delta L$ becomes 0.15, if B is 0.42 cm^2 and D is 10^{-5} cm^2/sec. Then ΔC becomes 0.0045 g./cc., when ΔL is 0.3 cm., the same length as the depth of the solution. This value of ΔC corresponds to about 0.01 mol. fraction. At the practical condition the supplement of zinc would be faster, as there may occur convection and the concentration gradient is not linear.

(C) Concentration Change due to Vaporization.—In one run 1 to 2 mg. of zinc effuses out. This affects the concentration by 0.003 at 0.05 and 0.0015 at 0.1 respectively in mole fraction. Then this effect is not so severe except in a composition of high dilution, where the effusion time of one run is desirable to be short.

Results and Discussion

Vapor Pressure of Pure Zinc. For the purpose of determining the effective area of the effusion orifice, effusion velocity was measured with pure solid zinc. An example of the results is shown in Table I. By means of

Table I. Effusion velocity of solid pure zinc

T, °K	$P\times KA$* mmHg×cm^2	T, °K	$P\times KA$ mmHg×cm^2
613	4.663×10^{-6}	646	17.15×10^{-6}
621	6.678 〃	649	18.58 〃
625	9.575 〃	658	25.88 〃
635	11.71 〃	661	34.46 〃
636	12.27 〃		

* The geometrical area A is 7.566×10^{-3} cm^2.

the least square method, these values are expressed as a linear function of $1/T$ by

$$\log P\times(KA) = -6716/T + 5.649 \qquad (2)$$

The vapor pressure of solid zinc has been investigated by many workers. The most reliable value, which Barrow and his coworkers derived[1], is

$$\log P = 9.8253 - 0.1923\log T - 0.2623\times10^{-3}T - 6862.5/T \qquad (3)$$

Comparing Eq. 2 with Eq. 3, the effective area KA of the orifice is calculated as 0.5735 mm^2. The geometrical area (A) was 0.7566 by microscopic measurement. The ratio of these figures leads to 0.758 as the Clausing factor, which corresponds to 0.099 mm. of thickness of the orifice. Substituting the effective area in Eq. 2, it can be rewritten as

$$\log P = -6716/T + 8.891 \qquad (4)$$

The vapor pressure of liquid zinc can be calculated from Eq. 4 and the free energy change of solidification of zinc[3] as a function of temperature. Thus the vapor pressure at 625°K is 1.603×10^{-2} mmHg, which is used as the reference in derivation of activity of zinc in alloys.

Vapor Pressure of Zinc in Liquid Alloy.—At the range of high content of zinc, zinc separates as solid matter over the temperature range where vapor pressure is appropriate in magnitude for the effusion method. The present measurement has covered up to 0.4 of mole fraction of zinc. Measured values are summarized in Table II, and plotted against reciprocal temperature in Fig. 2. The activity of zinc at 625°K, calculated from the above-mentioned values and 1.603×10^{-2} mmHg of

Table II. Vapor pressure of zinc in liquid tin-zinc system

X_{Zn}	T, °K	P_{Zn} mmHg $\times10^3$	X_{Zn}	T, °K	P_{Zn} mmHg $\times10^3$
0.027	645	2.99		659	18.1
	650	3.50		671	25.4
	660	4.31		686	40.5
	665	5.67	$\log P = -5976/T + 7.312$		
	675	6.09	0.252	615	6.08
	681	8.43		625	8.62
	685	8.90		636	11.9
$\log P = -5206/T + 5.546$				650	20.1
0.104	645	7.44	$\log P = -5822/T + 7.249$		
	655	10.1	0.364	597	4.11
	665	12.2		604	5.57
	670	15.0		606	5.74
	688	25.9		613	6.77
$\log P = -5432/T + 6.286$				621	9.15
0.150	616	4.34		625	12.2
	621	4.78		627	11.5
	626	5.83		635	13.9
	640	8.77		651	26.6
	640	9.95		659	34.8
	650	12.8	$\log P = -5769/T + 7.273$		
	652	13.5			

3) J. Lumsden, "Thermodynamics of Alloys", Institute of Metals, London (1952), p. 140.

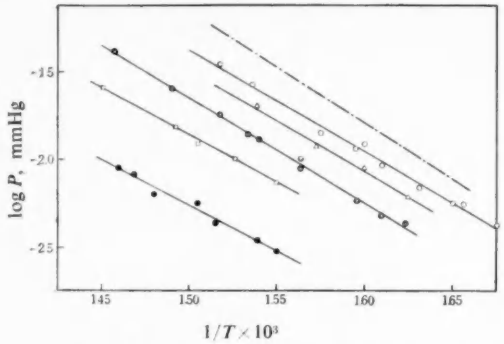


Fig. 2. Relation between logarithm of vapor pressure and reciprocal temperature.

---- liquid pure zinc ◎ $X_{Zn}=0.150$
○ $X_{Zn}=0.027$ □ 〃 0.252
△ 〃 0.104 ● 〃 0.364

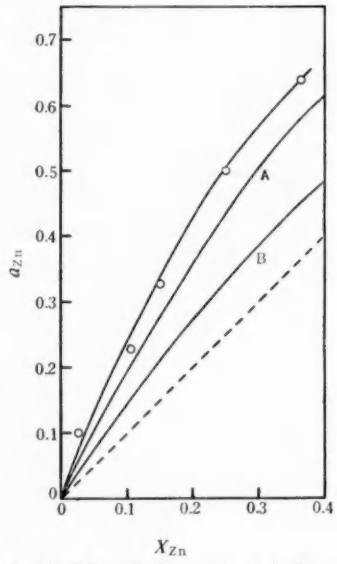


Fig. 3. Activity of zinc: open circle, present work at 625°K, line A, Taylor's value at 650°C, and line B, Jellinek's value at 700°C.

pure liquid zinc, is shown in Fig. 3. On this system Taylor[4] determined activity by e.m.f. method at 400 to 600°C, and Burmeister and Jellinek[5] measured vapor pressure of zinc by the transpiration method at a temperature range of 684 to 785°C. Their results are also shown in Fig. 3.

The thermodynamic property of alloys can be appropriately given in terms of excess function, where solutions are classified as ideal,

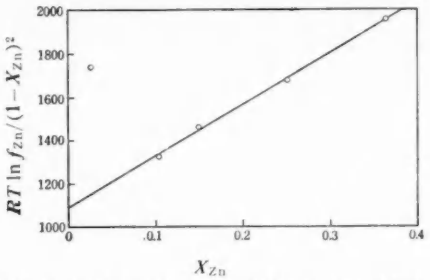


Fig. 4. Relation between $RT\ln f_{Zn}/(1-X_{Zn})^2$ and X_{Zn}.

regular or sub-regular ones. Wittig and his coworkers[6] have found that the heat of solution of this system behaves as a sub-regular solution as far as enthalpy is concerned. In Fig. 4 $RT\ln f_{Zn}/(1-X_{Zn})^2$ is plotted against concentration of zinc. All points are on a straight line

$$\frac{RT\ln f_{Zn}}{(1-X_{Zn})^2}=2370\,X_{Zn}+1090 \qquad (5)$$

One point at $X=0.027$ deviates from this line, probably because of the uncertainty of concentration. It would be worth while to find what these figures mean when this system is regarded as a sub-regular solution. By definition[7] excess free energy of solution is related to concentration by

$$\frac{G^e}{X_{Zn}X_{Sn}}=A^0+(X_{Sn}-X_{Zn})A^1 \qquad (6)$$

where A^0 and A^1 are constants. From this equation one can derive a formula for the excess chemical potential, defined as a difference between partial molar free energy of solution and ideal partial molar free energy of solution,

$$\mu^e_{Zn}/X^2_{Sn}=RT\ln f_{Zn}\times 1/X^2_{Sn}=A^0+(1-4X_{Zn})A^1 \qquad (7)$$

Comparing Eq. 7 with Eq. 5, values of As are given,

$$A^0=1680 \quad \text{and} \quad A^1=-590$$

Taylor's data at equal range of concentration lead to $A^0=1660$ and $A^1=-430$. Accounting for the temperature dependence of these quantities, two sets of data are in good agreement within experimental error.

This sub-regular behavior has not yet been completely interpreted. In the case of molecular liquid solutions, Hildebrand[8] succeeded in explaining energetic asymmetry by using

4) N. W. Taylor, *J. Am. Chem. Soc.*, **45**, 2865 (1923).
5) E. Burmeister and K. Jellinek, *Z. phys. Chem.*, **A165**, 121 (1933).
6) F. E. Wittig, *Z. Electrochem.*, **63**, 327 (1959).
7) H. Hardy, *Acta Met.*, **1**, 202 (1952).
8) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes", Reinhold, New York (1952), p. 109.

volume fraction in place of mole fraction. In the present case this correction is not enough. Kleppa[9] and Wittig[6] pointed out the correlation of the energetic asymmetry with valence electron concentration from the experimental data of many alloy systems. Recently some investigators[10] paid attention to the cohesive energy of metals in light of metallic characteristics and considered what happened on mixing. Shimoji[11] discussed the excess energy of binary alloys by using the cellular approximation for metals and explained energetic asymmetry on mixing, not by the simple volume effect, but by the changes of the energy due to the boundary correction, Fermi energy, interelectronic energy, closed shell repulsive energy, polarization energy etc. It is interesting to compare the calculation with the present data. In the moderately dilute range, integral heats of mixing can be expanded in a power series of the mole fraction of the solute,

$$\Delta H^M = P_1 x_2 + P_2 x_2^2 + \cdots\cdots \quad (8)$$

According to Shimoji the ratio $-P_2/P_1$ is 0.4 in the zinc dilute portion of tin-zinc system. From Eq. 8 one obtains the relative partial molar enthalpy as

$$\overline{\Delta H}_2 = P_1 + 2P_2 x_2 + \cdots\cdots \quad (9)$$

The corresponding equation can be derived from the present data by the following equation, provided that the partial molar excess entropy is known,

$$\overline{\Delta H}_{Zn} = \mu^e{}_{Zn} + T\overline{\Delta S}^e{}_{Zn} \quad (10)$$

Assuming that the excess entropy is mainly due to volume difference, partial molar excess entropy of solution of zinc can be calculated by free volume model[8]:

$$\overline{\Delta S}^e{}_{Zn} = -R\left[\ln \varphi_{Zn} + \varphi\left(1 - \frac{V_{Zn}}{V_{Sn}}\right) - \ln X_{Zn}\right] \quad (11)$$

where φ is the volume fraction and V is the molar volume. Replacing φ by the mole fraction and molar volumes, one obtains

$$\overline{\Delta S}^e{}_{Zn} = 1.05 - 1.31\, X_{Zn} + \cdots\cdots \quad (12)$$

where 16.9 and 9.9 is used as molar volumes of tin and zinc. On the other hand, Eq. 5 is rewritten as

$$\mu^e{}_{Zn} = 1090 + 190 X_{Zn} + \cdots\cdots \quad (13)$$

From Eqs. 12 and 13 the partial molar enthalpy of zinc at 625°K is

$$\overline{\Delta H}_{Zn} = 1750 - 630 X_{Zn} + \cdots\cdots \quad (14)$$

giving 1750 and -315 cal./mol. for P_1 and P_2 respectively. Then the present value 0.18 for $-P_2/P_1$ seems to agree with 0.4 (Shimoji's value) in deviation from $P_2/P_1 = -1$ (regular solution). The experimental results about ternary solutions will be reported in the next paper.

Summary

The vapor pressure of zinc in liquid tin-zinc alloys has been measured by Knudsen's effusion method. Application of this method to liquid alloys has been found to be successful. Observed activity coefficients of zinc are discussed in relation to theoretical calculations. The deviation from the regular solution model has been interpreted in terms of the cellular approximation as well as the volume difference effect.

The authors are indebted to Dr. M. Shimoji for his valuable discussion.

Department of Chemistry
Faculty of Science
Hokkaido University, Sapporo

9) O. J. Kleppa, *Acta Met.*, **6**, 225 (1958).
10) J. Friedel, *Phil. Mag.*, **43**, 153 (1952); J. H. O. Varley, *ibid.*, **45**, 887 (1954).
11) M. Shimoji, *J. Phys. Soc. Japan*, **14**, 1525 (1959).

Studies on the Decomposition of Ammonia and Hydrazine by High Frequency Discharge

By Saku TAKAHASHI

(Received February 20, 1960)

The chemical reaction under high frequency discharge has been studied and it has been found that the energy consumed in the reaction is roughly proportional to the frequency of the applied electric current[1]. However, from the standpoint of reaction rate, it is highly questionable whether the rate of reaction under high frequency discharge would be affected by the frequency of the applied electric current or not. In order to obtain information concerning the reactions under high frequency discharge, the selectivities of frequencies to the reactions in the decomposition of both ammonia and hydrazine vapour have been studied.

Experimental Procedures

The decomposition of ammonia and also of hydrazine under high frequency discharge were carried out in a closed vessel shown in Fig. 1. The volume of the glass vessel, cylindrical in shape, of which the diameter was 7 cm., was approximately 1000 cc. A single electrode was inserted into this vessel at the bottom and high frequency electric current was applied to this electrode. The electric discharge occurred at the top of this electrode.

The frequencies of electric current used in these experiments were 100 and 250 MC. For the purpose of keeping their power applied on these reactions at a definite value, all the electric conditions of a generator were constantly fixed in every case.

The ammonia, hydrazine, nitrogen and hydrogen used in these experiments were purified by ordinary methods. The quantities of ammonia and hydrazine in the reaction vessel were expressed by the partial pressures in the reaction vessel at 25°C. The initial pressure of ammonia was from 50 to 250 mmHg and that of hydrazine was from 3 to 10 mmHg.

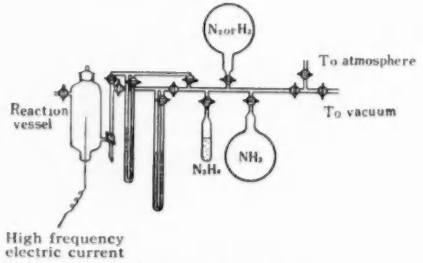


Fig. 1. Apparatus

Results and Discussion

In these experiments, the amounts of reactant were plotted against the reaction time. Several experiments with additional hydrogen or nitrogen were also carried out. From these results, the rate of the reaction was expressed with the amount of the reactant decomposed in a certain reaction time.

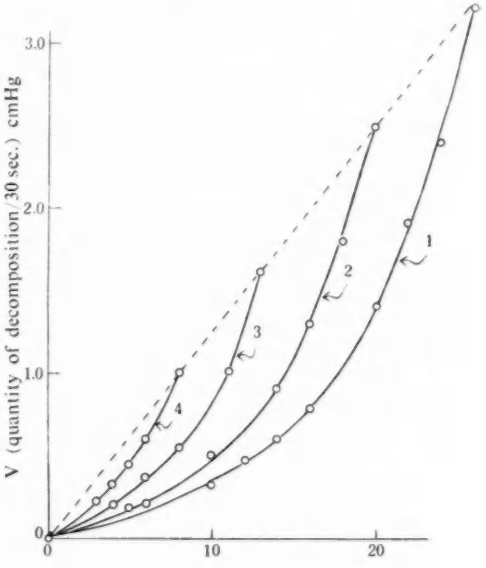


Fig. 2. Influence of initial pressure on reaction rate under 100 MC frequency discharge. Showing that the initial reaction rate is proportional to the amount of ammonia and the decomposition products retard the reaction.

NO.	$[P_{NH_3}]_0$, cmHg
1	26.0
2	20.0
3	13.0
4	8.0

1) E. Briner et al., *Helv. Chim. Acta*, **14**, 534 (1931); **18**, 1468 (1935); **19**, 287 (1936); **28**, 714 (1945); **30**, 105 (1947).

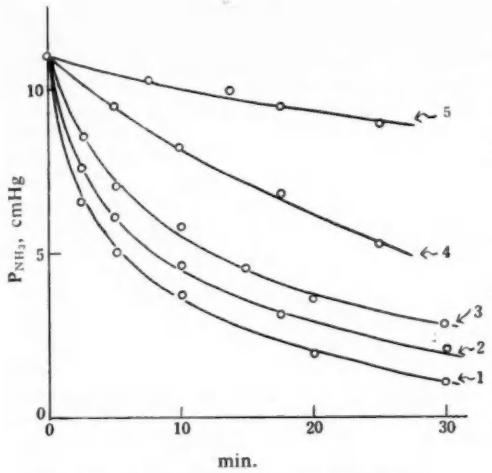


Fig. 3. Effect of hydrogen on decomposition of ammonia under 100 MC frequency discharge. Plots of amount of ammonia against reaction time.

$[P_{NH_3}]_0$; 11.0 cmHg

NO.	$[H_2]_0$, cmHg
1	0
2	3.50
3	14.30
4	25.80
5	32.80

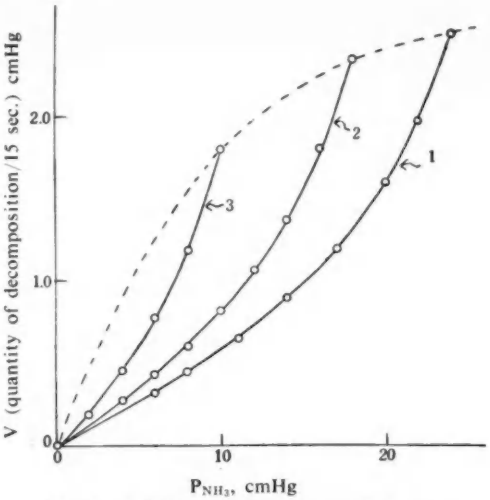


Fig. 5. Influence of initial pressure on reaction rate under 250 MC frequency discharge. Showing that the initial reaction is an intermediate type between the zero and the 1st order reaction and the reaction is retarded by the decomposition products.

NO.	$[P_{NH_3}]_0$, cmHg
1	24.0
2	18.0
3	10.0

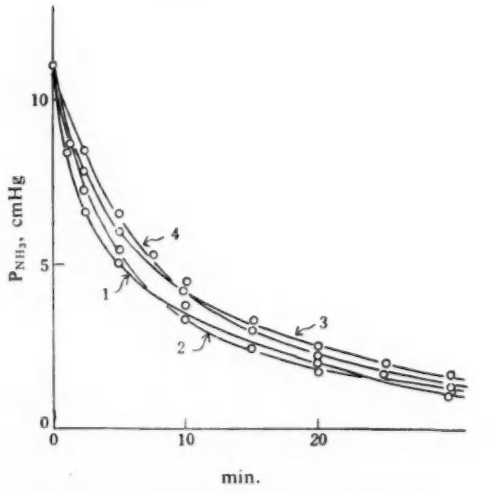


Fig. 4. Effect of nitrogen on decomposition of ammonia under 100 MC frequency discharge. Plots of amount of ammonia against reaction time.

$[P_{NH_3}]_0$; 11.0 cmHg

NO.	$[N_2]_0$, cmHg
1	0
2	3.10
3	11.80
4	33.80

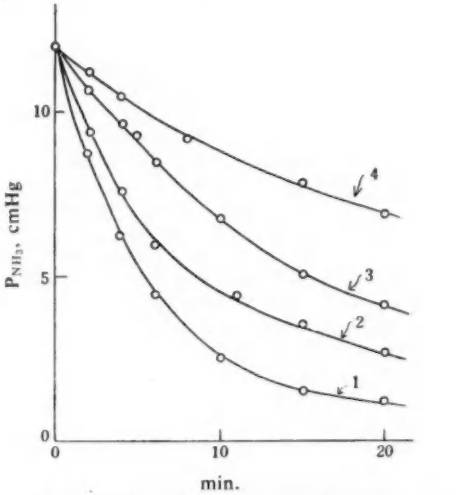


Fig. 6. Effect of hydrogen on decomposition of ammonia under 250 MC frequency discharge. Plots of amount of ammonia against reaction time.

$[P_{NH_3}]_0$; 12.0 cmHg

NO.	$[P_{H_2}]_0$, cmHg
1	0
2	3.0
3	9.0
4	12.0

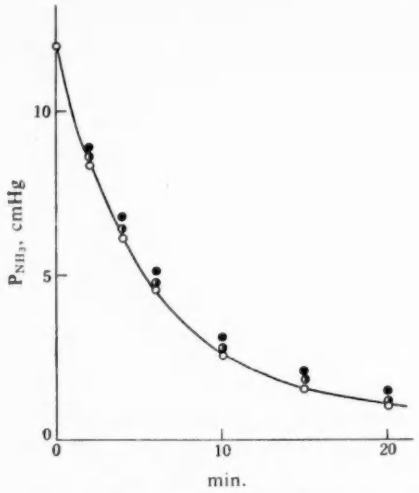


Fig. 7. Effect of nitrogen on decomposition of ammonia under 250 MC frequency discharge. Plots of amount of ammonia against reaction time.
$[P_{NH_3}]_0$; 12.0 cmHg
$[P_{N_2}]_0$, cmHg
○····· 0
◑····· 6.00
●·····10.50

Decomposition of Ammonia. The decomposition products were analysed by gas chromatography. They were nitrogen, hydrogen and hydrazine. The main products were nitrogen and hydrogen. The amount of hydrazine produced was so small that the effect caused by the hydrazine on this reaction may be ignored.

On the decomposition under 100 MC frequency discharge, it is shown in Fig. 2 that the initial stage of the reaction was of the 1st order and that the retardation by both nitrogen and hydrogen was observed. Comparing Fig. 3 with Fig. 4, it is seen that the amount of ammonia decomposed in a definite time decreases according to the quantity of hydrogen added, while the nitrogen added exhibits no effects on the rate of ammonia decomposition. Under 250 MC frequency discharge, it is known from Fig. 5 that the initial reaction is not of the 1st order, but it is an intermediate type between the zero and 1st order reactions, and comparing Fig. 6 with Fig. 7, it may be seen that the overall reaction is retarded by hydrogen.

The molecules in electric discharge are excited by a collision with an impacting electron and change to an excited molecule or a positive ion. It is considered that both a positive ion and an excited molecule are possible agents in the chemical reaction. If excited molecules were responsible, the reaction should be pressure sensitive, for it may be expected that the concentration of excited molecules would decrease with pressure. The outstanding feature of the experiment in electric discharge is that the reaction is directly proportional to the discharge current and it is independent of pressure over a large range of values. Furthermore, it has been observed in the studies[2] with electrons of controlled speed that the reaction hardly occurs below the ionization potential of the gas. These experimental results favor an ionic reaction in electric discharge. Upon neutralization of a positive ion, the entire energy of ionization available may serve as activation energy for chemical processes or else the molecule will return to the normal state after a short average life with the emission of radiation[3]. In a spectroscopic investigation[4], on high frequency discharge, it has been noticed that, in a discharge tube, a molecule with one charge comes to be clearly observed as the frequency of electric current increases. This phenomenon shows one of the specific properties of high frequency discharge and from this fact it is presumed that the life-time and number of positive charge moleculs produced in a discharge tube tend to increase with the frequency of the electric current.

Thus, one accounts for the kinetics of reactions by the following series of reactions:

$$NH_3 \xrightarrow{k_1} NH_3^+ \quad \text{(in electric discharge)}$$

$$NH_3^+ \xrightarrow{k_2} NH_3^*$$

$$NH_3^* \xrightarrow{k_3} \frac{1}{2}N_2 + \frac{3}{2}H_2$$

$$NH_3^+ \xrightarrow{k_4} NH_3 + E$$

$$NH_3^+ + H_2 \xrightarrow{k_5} [NH_3^+ \cdot H_2] \longrightarrow NH_3 + H_2 + E_1$$

$$NH_3^+ + NH_3 \xrightarrow{k_6} [NH_3^+ \cdot NH_3] \longrightarrow NH_3 + NH_3 + E_2$$

In these reactions, it is difficult to understand strictly the behaviour of hydrogen molecules, but from the results obtained in this experiment it is supposed that hydrogen has the greatest probability of deactivation of all ionized molecules. If the life-time of NH_3^+ is long, it is known that, as the results of several collisions between hydrogen and the ionized

2) C. H. Kunsman, *Phys. Rev.*, **31**, 307 (1928).
3) G. Glockler, "The Electrochemistry of Gases and other Dielectrics", John Wiley & Sons, Inc., New York (1939), p. 430.
4) W. Jones, *Proc. Roy. Soc.*, **A127**, 511 (1930); L. Henry, *J. Phys. Chem.*, **34**, 2792 (1930).

molecule, the ionized molecule loses its excessive energy and becomes a normal molecule, while hydrogen becomes an activated molecule. Applying the steady state assumption, one arrives at expression 1 for the rate of decomposition.

$$\frac{d[NH_3^+]}{dt} = k_1[NH_3] - k_2[NH_3^+] - k_4[NH_3^+] - k_5[NH_3^+][H_2] - k_6[NH_3^+][NH_3] = 0$$

$$[NH_3^+] = \frac{k_1[NH_3]}{k_2 + k_4 + k_5[H_2] + k_6[NH_3]}$$

$$\frac{d[NH_3^*]}{dt} = k_2[NH_3^+] - k_3[NH_3^*] = 0$$

$$[NH_3^*] = \frac{k_2}{k_3}[NH_3^+]$$

$$V = k_3[NH_3^*] = k_2[NH_3^+] = \frac{k_1k_2[NH_3]}{k_2 + k_4 + k_5[H_2] + k_6[NH_3]} \quad (1)$$

When a hydrogen molecule does not exist in a reaction vessel, the rate of reaction is expressed as follows and this formula expresses the relation between the initial rate V_0 and the concentration of ammonia.

$$V_0 = k_3[NH_3^*] = k_2[NH_3^+] = \frac{k_1k_2[NH_3]}{k_2 + k_4 + k_6[NH_3]} \quad (2)$$

Using expressions 1 and 2, the following relations are obtained.

$$\frac{V_0 - V}{V} = \frac{k_5[H_2]}{k_2 + k_4 + k_6[NH_3]} = \Theta$$

$$\frac{k_2 + k_4}{k_5} + \frac{k_6}{k_5}[NH_3] = \frac{[H_2]}{\Theta} \quad (3)$$

If the life-time of NH_3^+ is short, the k_6 process may be neglected and the rate of decomposition is approximated as follows:

$$V = \frac{k_1k_2[NH_3]}{k_2 + k_4 + k_5[H_2]} \quad (4)$$

$$\frac{k_2 + k_4}{k_1k_2} + \frac{k_5}{k_1k_2}[H_2] = \frac{[NH_3]}{V} \quad (5)$$

Using the results shown in Figs. 2 and 5, the plots of NH_3/V vs. H_2 and H_2/Θ vs. NH_3 are shown in Figs. 12 and 13, respectively. A linear relation between NH_3/V and H_2 or H_2/Θ and NH_3 is clearly shown in these figures, being independent of the initial concentration of ammonia, and the agreement between the experiment and the calculation is reasonable.

Decomposition of Hydrazine.—The decomposition products of this reaction are nitrogen and hydrogen and ammonia is not produced. In this reaction, comparing Fig. 8 with Fig. 9

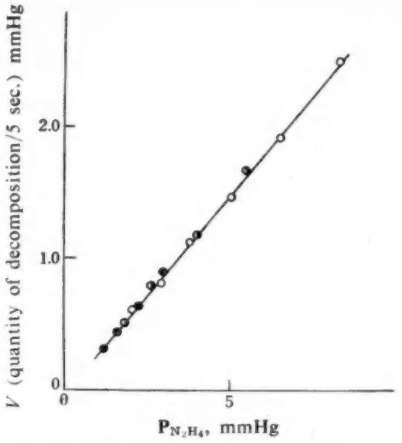


Fig. 8. Decomposition of hydrazine under 100 MC frequency discharge. Plots of reaction rate against hydrazine concentration.

$[P_{N_2H_4}]_0$, mmHg
○……8.40
◑……5.50
●……3.00

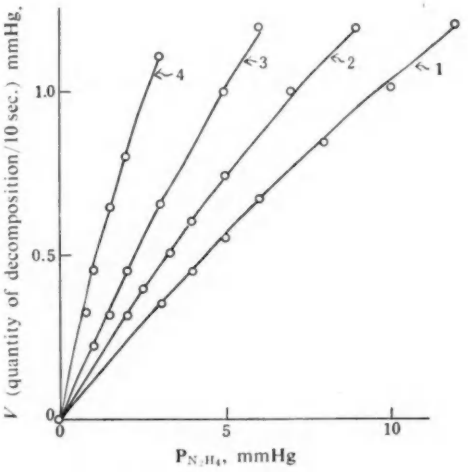


Fig. 9. Influence of initial pressure on reaction rate under 250 MC frequency discharge. Showing that the initial reaction is zero order and the reaction is retarded by the decomposition products.

NO.	$[P_{N_2H_4}]_0$, mmHg
1	12.0
2	9.0
3	6.0
4	3.0

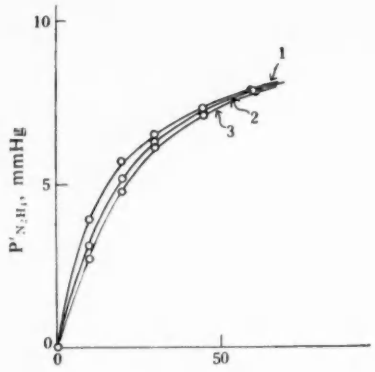


Fig. 10. Effect of nitrogen and hydrogen on decomposition of hydrazine under 100 MC frequency discharge. Plots of amount of hydrazine decomposed against reaction time.

$[P_{N_2H_4}]_0$; 8.40 mmHg

NO.	$[P_{H_2}]_0$, mmHg	$[P_{N_2}]_0$, mmHg
1	0	0
2	15.0	0
3	0	15.0

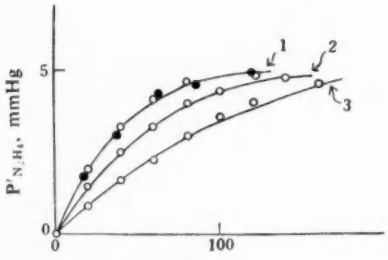


Fig. 11. Effect of nitrogen and hydrogen on decomposition of hydrazine under 250 MC frequency discharge. Plots of amount of hydrazine decomposed against reaction time.

$[P_{N_2H_4}]_0$; 5.0 mmHg

NO.	$[P_{N_2}]_0$, mmHg	$[P_{H_2}]_0$, mmHg
1 ○	0	0
1 ●	0	6.0
2	6.0	0
3	9.0	0

it can be shown that the rate of decomposition under high frequency discharge varies with the values of frequencies of the applied electric current. The reaction under the frequency 100 MC is a 1st order reaction, but under the frequency 250 MC the initial rate of decomposition is of zero order. Moreover, as is seen in Figs. 10 and 11, the hydrogen produced in the course of the decomposition does not retard the rate of decomposition

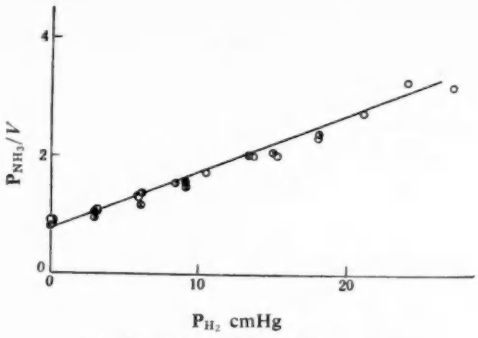


Fig. 12. Plots of P_{NH_3}/V vs. P_{H_2}.

$[P_{NH_3}]_0$, cmHg	$[P_{NH_3}]_0$, cmHg
○……26.0	◑……20.0
⊗……13.0	●…… 8.0

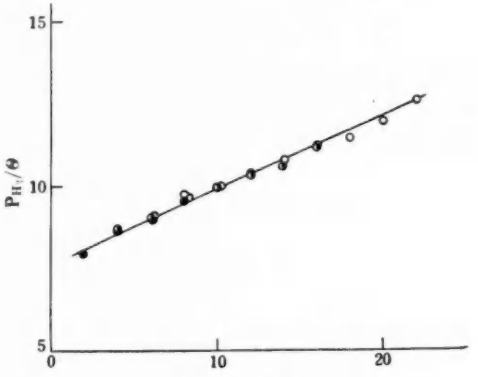


Fig. 13. Plots of P_{H_2}/θ vs. P_{NH_3}.

$[P_{NH_3}]_0$, cmHg	$[P_{NH_3}]_0$, cmHg
○……24.0	◑……18.0
●……10.0	

under the former condition, but it moderately retards the rate of reaction under the latter condition. From these results, it is possible to explain the reaction processes as follows:

$$N_2H_4 \xrightarrow{k_1} N_2H_4^+ \text{ (in electric discharge)}$$

$$N_2H_4^+ \xrightarrow{k_2} N_2H_4^*$$

$$N_2H_4^* \xrightarrow{k_3} N_2 + 2H_2$$

$$N_2H_4^+ \xrightarrow{k_4} N_2H_4 + E$$

$$N_2H_4^+ + H_2 \xrightarrow{k_5} [N_2H_4^+ \cdot H_2] \longrightarrow N_2H_4 + H_2 + E_1$$

$$N_2H_4^+ + N_2H_4 \xrightarrow{k_6} [N_2H_4^+ \cdot N_2H_4] \longrightarrow N_2H_4 + N_2H_4 + E_2$$

Under the frequency 100 MC, if the lifetime of $N_2H_4^+$ is short, it is supposed that $N_2H_4^+$ cannot be deactivated by the collision with H_2 or N_2H_4. In this case, applying the usual steady state assumption, expression 6 for the rate of decomposition is obtained.

$$\frac{d[N_2H_4^+]}{dt} = k_1[N_2H_4] - k_2[N_2H_4^+] - k_4[N_2H_4^+] = 0$$

$$[N_2H_4^+] = \frac{k_1[N_2H_4]}{k_2+k_4}$$

$$\frac{d[N_2H_4^*]}{dt} = k_2[N_2H_4^+] - k_3[N_2H_4^*] = 0$$

$$[N_2H_4^*] = \frac{k_2}{k_3}[N_2H_4^+]$$

$$V = k_3[N_2H_4^*] = \frac{k_1k_2}{k_2+k_4}[N_2H_4] \qquad (6)$$

Under the frequency 250 MC, if the lifetime of $N_2H_4^+$ becomes longer with the increase of frequency of electric current, it is supposed that $N_2H_4^+$ comes to be deactivated by each molecule of hydrogen and hydrazine. In this case, the following equations are obtained:

$$\frac{d[N_2H_4^+]}{dt} = k_1[N_2H_4] - k_2[N_2H_4^+] - k_4[N_2H_4^+] - k_5[N_2H_4^+][H_2] - k_6[N_2H_4^+][N_2H_4] = 0$$

$$[N_2H_4^+] = \frac{k_1[N_2H_4]}{k_2+k_4+k_5[H_2]+k_6[N_2H_4]}$$

$$\frac{d[N_2H_4^*]}{dt} = k_2[N_2H_4^+] - k_3[N_2H_4^*] = 0$$

$$[N_2H_4^*] = \frac{k_2}{k_3}[N_2H_4^+]$$

$$V = k_3[N_2H_4^+] = \frac{k_1k_2[N_2H_4]}{k_2+k_4+k_5[H_2]+k_6[N_2H_4]} \qquad (7)$$

In this decomposition, as the value of hydrogen produced in the course of the decomposition is equal to $2([N_2H_4]_0 - [N_2H_4])$ the following equations are derived.

$$V = \frac{k_1k_2[N_2H_4]}{k_2+k_4+2k_5[N_2H_4]_0+(k_6-2k_5)[N_2H_4]}$$

$$\frac{[N_2H_4]}{V} = \frac{1}{k_1k_2}\{(k_2+k_4+2k_5[N_2H_4]_0) + (k_6-2k_5)[N_2H_4]\} \qquad (8)$$

where, $[N_2H_4]_0$ is the initial concentration of hydrazine. Using the results shown in Fig. 9, N_2H_4/V is plotted against N_2H_4 as shown in Fig. 14. As is obvious from these figures, the agreement between the experiment and the calculation is satisfactory.

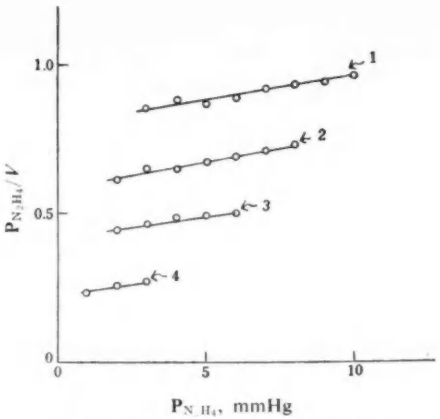


Fig. 14. Plots of $P_{N_2H_4}/V$ vs. $P_{N_2H_4}$.

NO.	$[P_{N_2H_4}]_0$, mmHg
1	12.0
2	9.0
3	6.0
4	3.0

Summary

1) The decomposition of both ammonia and hydrazine were carried out under high frequency discharge and the effects of frequency on the chemical reactions were investigated. The frequencies of electric current were 100 and 250 MC.

2) The effects of frequency appeared clearly on the decomposition of hydrazine: under 100 MC frequency discharge the decomposition was a 1st order reaction, while under 250 MC it was approximately zero order reaction, and the overall reaction was retarded moderately by the hydrogen produced in the course of the reaction.

3) As for the decomposition of ammonia, in any case, the reactions were retarded by hydrogen. Under 100 MC frequency discharge the reaction was 1st order, while under 250 MC it was a fractional order reaction.

The author wishes to express her thanks to Professor M. Suzuki for his exceedingly kind direction throughout this work. The author also thanks Professor K. Tamaru of the University of Yokohama for his helpful advice.

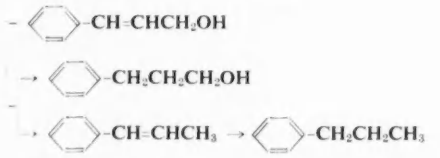
Department of Chemistry
Defense Academy
Yokosuka

Hydrogenation and Hydrogenolysis. IV[1]. *Catalytic Reductions of Cinnamyl Alcohols and 3-Phenylpropargyl Alcohol**

By Shigeo NISHIMURA, Takeru ONODA and Akiya NAKAMURA

(Received May 9, 1960)

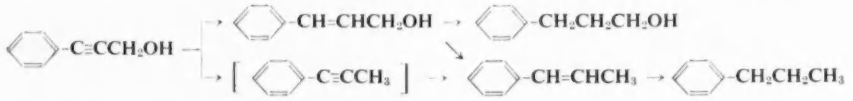
Cinnamyl alcohol may be catalytically reduced either to 3-phenyl-1-propanol, absorbing 1 mole of hydrogen, or to propylbenzene through propenylbenzene, absorbing 2 moles of hydrogen, as far as the hydrogenation is concerned with the side chain:



The reduction with nickel[2,3], cobalt[2] and copper[4] catalysts of Raney type gives phenylpropanol exclusively. Straus and Grindel[5] reduced cinnamyl alcohol with a palladium catalyst prepared by reducing palladium chloride with hydrogen in acetone, and obtained a mixture of propylbenzene (18%) and phenylpropanol (55%) with the absorption 1.38 moles of hydrogen. Baltzly and Buck[6] obtained about equal moles of the two compounds with the use of palladized charcoal in ethanol. Waser[7] obtained cyclohexylpropanol quantitatively by the reduction with a platinum black without using any solvent. Tuley and Adams[8] hydrogenated cinnamyl alcohol to phenylpropanol quantitatively in ethanol in the presence of platinum oxide and a small amount of ferrous chloride.

Different results of previous works on the hydrogenation of cinnamyl alcohol seem to be closely related to solvents and to metals and the methods of preparation of the catalysts. As reported previously[9,10], with platinum oxide as the catalyst, the hydrogenolysis of the C–O linkage with a bouble bond in β,γ- or α,β-position is much more favored than the hydrogenation of the double bond in acidic media. On the other hand, the double bond can be hydrogenated with little hydrogenolysis or none under neutral or slightly acidic conditions. In the present investigation, the influence of solvents on the hydrogenation and hydrogenolysis of cinnamyl alcohol was re-examined in detail with platinum, palladium, rhodium and rhodium-platinum catalysts.

3-Phenylpropargyl alcohol may be catalytically reduced either to 3-phenyl-1-propanol through *cis*-cinnamyl alcohol, absorbing 2 moles of hydrogen, or to propylbenzene, through *cis*-cinnamyl alcohol or through propynylbenzene, absorbing 3 moles of hydrogen:



In order to know whether the hydrogenolysis would occur or not before the reduction of the triple bond to the double bond, the catalytic reduction of 3-phenylpropargyl alcohol and of the intermediate *cis*-cinnamyl alcohol was investigated with Adams platinum oxide as a catalyst.

Experimental

Substrates.—*Cinnamyl Alcohol* (*trans*). –A commercial preparation was treated with aluminum ethoxide and absolute ethanol followed by hydrolysis with sodium hydroxide solution and extraction with ether[11], and then fractionally distilled twice under reduced pressure. B. p. 139.5~140.5°C/16 mmHg; n_D^{21} 1.5820.

1) Part III of this series: S. Nishimura, This Bulletin, 33, 566 (1960).

* Presented at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1960.

2) B. V. Aller, *J. Appl. Chem.*, **8**, 492 (1958).

3) Cinnamyl alcohol absorbed 0.98 mole of hydrogen in ethanol under ordinary conditions with T-4 Raney nickel (S. Nishimura, This Bulletin, **32**, 61 (1959)).

4) J. Jadot and R. Braine, *Bull. soc. roy. sci. Liége*, **25**, 62 (1956); *Chem. Abstr.*, **50**, 16651h (1956).

5) F. Straus and H. Grindel, *Ann.*, **439**, 276 (1924).

6) R. Baltzly and J. S. Buck, *J. Am. Chem. Soc.*, **65**, 1984 (1943).

7) E. Waser, *Helv. Chim. Acta*, **8**, 117 (1925).

8) W. F. Tuley and R. Adams, *J. Am. Chem. Soc.*, **47**, 3061 (1925).

9) S. Nishimura and K. Mori, This Bulletin, **32**, 103 (1959). Also cf. C. W. Shoppee et al., *J. Chem. Soc.*, **1957**, 3107.

10) S. Nishimura, This Bulletin, **32**, 1155 (1959).

TABLE I. MOLES OF HYDROGEN ABSORBED BY CINNAMYL ALCOHOL AT ORDINARY TEMPERATURE AND PRESSURE[a]

Catalyst*	Solvent			
	EtOH, 20 cc.	AcOH, 20 cc.	EtOH, 20 cc.+ 3N HCl, 0.1 cc.	AcOH, 20 cc.+ 3N HCl, 0.1 cc.
Pt oxide	1.03	1.31	1.60	1.79
Pd oxide	1.02	1.10	1.21	1.63
Rh-Pt (1 : 1) oxide		1.10		1.73**
Rh-Pt (2 : 1) oxide		1.07		1.71**
Rh-Pt (3 : 1) oxide	0.94	1.04	1.25	1.66**
Pd-on-carbon (I)	0.99		1.22	
Pd-on-carbon (II)	1.10	1.07	1.23	1.57
Rh-on-carbon (II)	1.24	1.14	1.33	1.45

a) 1.342 g. (0.01 mol.) of cinnamyl alcohol was hydrogenated with 50 mg. of the oxide or 600 mg. of the supported catalysts each time.

* For the notations attached to the catalysts, see the experimental part.

** These are approximate values, because the further hydrogenation of the benzene nucleus made obscure the completion of the reduction of the side chain.

Cinnamyl Acetate (trans).—Cinnamyl alcohol was refluxed with acetic anhydride and the product was fractionated twice under reduced pressure. B. p. 140~141°C/16 mmHg ; n_D^{21} 1.5439.

3-Phenylpropargyl Alcohol.—This compound was prepared by passing mixed nitrogen and formaldehyde gases into an ethereal solution of phenylethynylmagnesium bromide prepared from phenylacetylene and ethylmagnesium bromide[12]. The product was distilled twice under reduced pressure. B. p. 150°C/30 mmHg ; n_D^{20} 1.5845.

cis-Cinnamyl Alcohol.—3-Phenylpropargyl alcohol was partially hydrogenated in ethyl acetate with 5% palladium-on-barium sulfate[13] poisoned with a few drops of quinoline. The rate of the hydrogenation became markedly slow after the absorption of 0.97 mole of hydrogen. The product was distilled twice under reduced pressure. B. p. 125°C/14 mmHg (lit.[13] 125.5°C/13 mmHg); n_D^{16} 1.5745 (lit.[13] n_D^{15} 1.573). It was confirmed by the infrared adsorption that the alcohol thus prepared contained, if any, less than 10% of its trans isomer and less than 3% of 3-phenylpropargyl alcohol*.

Catalysts.—Platinum oxide was prepared by fusion of ammonium chloroplatinate with sodium nitrate according to the method of Bruce[14].

Palladous oxide was prepared by the fusion of palladium chloride with sodium nitrate according to the method of Shriner and Adams[15].

Rhodium-platinum oxide catalysts were prepared by fusion of the mixtures of rhodium chloride and chloroplatinic acid or ammonium chloroplatinate with sodium nitrate as reported previously[1]. The figures in parentheses in Table I indicate the ratios of rhodium to platinum by the weights of the metals.

Palladium-on-carbon (I) (5% Pd) was prepared by reducing a palladium chloride solution with aqueous formaldehyde and sodium hydroxide[16].

Palladium-on-carbon (II) and rhodium-on-carbon (II) (5% Pd or Rh) were prepared by reducing palladium and rhodium chloride solutions with hydrogen with the addition of sodium acetate[17].

Solvents.—*Acetic Acid.*—Glacial acetic acid of Wakō Pure Chemical Industries G. R. grade was used without further purification.

Ethanol.—Commercial 95% ethanol was used after distillation.

Hydrogenation.—Hydrogenation was carried out at room temperature (20~25°C) and atmospheric pressure. After the catalyst was shaken with hydrogen in 15 cc. of the solvent until no more hydrogen was absorbed, the substance, dissolved in 5 cc. of the solvent, was added. The mixture was shaken with hydrogen at about 350~400 oscillations per minute. In using rhodium-platinum oxide catalysts, hydrochloric acid was added after the oxide was reduced to the metal, since the presence of hydrochloric acid greatly retarded the reduction of the oxide.

Results and Discussion

Catalytic Reduction of Cinnamyl Alcohol (trans).—The effects of solvents on the hydrogenation of cinnamyl alcohol are summarized in Table I in the moles of hydrogen absorbed per mole of cinnamyl alcohol. As expected from previous results, little hydrogenolysis or none occurred in neutral ethanolic solution[18]

11) H. Meerwein and R. Schmidt, *Ann.*, **444**, 221 (1925).
12) H. H. Guest, *J. Am. Chem. Soc.*, **47**, 860 (1925).
13) Cf. M. Bourguel, *Bull. soc. chim. France*, [4], **45**, 1083 (1929).
* The authors wish to thank Dr. H. Iwamura of this laboratory for his kind help in the measurement of infrared spectra.
14) W. F. Bruce, *J. Am. Chem. Soc.*, **58**, 687 (1936); R. Adams, V. Voorhees and R. L. Shriner, "Organic Syntheses", Col. Vol. 1, 2nd Ed., John Wiley & Sons, Inc., New York (1941), p. 463.
15) R. L. Shriner and R. Adams, *J. Am. Chem. Soc.*, **46**, 1683 (1924).
16) R. Mozingo, "Organic Syntheses", Col. Vol. 3, John Wiley & Sons, Inc., New York (1955), p. 685 (Method B).
17) Method D in Ref. 16.
18) The hydrogen uptake less than 1 mole with rhodium-platium (3 : 1) oxide in ethanol may be due to dimerization though it has not been investigated further.

TABLE II. EFFECT OF VARYING AMOUNTS OF ADDED HYDROCHLORIC ACID ON THE HYDROGEN UPTAKE BY CINNAMYL ALCOHOL[a]

Solvent	Hydrogen uptake mol./mol.
AcOH, 20 cc. + 3N HCl, 0.025 cc.	1.72
〃 , 0.05 cc.	1.78
〃 , 0.10 cc.	1.78
〃 , 0.15 cc.	1.79
〃 , 0.20 cc.	1.79

a) 1.342 g. (0.01 mol.) of cinnamyl alcohol was hydrogenated with 50 mg. of platinum oxide each time.

TABLE III. CATALYTIC REDUCTIONS OF CINNAMYL ACETATE AND CINNAMYL ALCOHOL[a]

Solvent	Hydrogen uptake mol./mol.	
	Cinnamyl acetate	Cinnamyl alcohol
AcOH, 20 cc.	1.30	1.31
EtOH, 20 cc. + 3N HCl, 0.1 cc.	1.50	1.60
AcOH, 20 cc. + 3N HCl, 0.1 cc.	1.80	1.79

a) 0.01 mol. of the substrate was hydrogenated with 50 mg. of platinum oxide each time.

except in hydrogenation with palladium-on-carbon (II) and rhodium-on-carbon (II), which were prepared from acidic media though washed with water many times and dried before use. Generally, the absorption of hydrogen increased in the following order with respect to the solvents; ethanol, acetic acid, ethanol with hydrochloric acid, and acetic acid with hydrochloric acid. This may be interpreted as the order of the abilities of the solvents as proton donors, which may become clearer by considering their conjugate acids, namely, $EtOH < AcOH < EtOH_2^+ < AcOH_2^+$[19], indicating that the hydrogenolysis is acid-catalyzed[20]. With respect to the catalysts, platinum oxide causes the greatest absorption of hydrogen[21], and rhodium added to platinum decreases the hydrogenolysis markedly. For instance, in acetic acid with hydrochloric acid, as much as 79% of cinnamyl alcohol is reduced to propylbenzene with platinum oxide. On the other hand, with rhodium-platinum (3 : 1) oxide only 4% is hydrogenolyzed in acetic acid, compared with 31% with platinum oxide in the same solvent.

Table II shows the effect of varying amounts of added hydrochloric acid on the hydrogen uptake by cinnamyl alcohol in acetic acid with platinum oxide as a catalyst. It is seen that a very small amount of hydrochloric acid is sufficient for the maximum absorption of hydrogen and further addition has little effect. It seems improbable that the greater absorption of hydrogen would result from the intermediate formation of cinnamyl acetate, because cinnamyl acetate absorbed no more hydrogen than cinnamyl alcohol in hydrogenation with platinum oxide as shown in Table III.

With respect to the activities of the three oxide catalysts, it may be said that the order was as follows; rhodium-platinum (3 : 1) oxide > palladous oxide > platinum oxide, though an accurate comparison was not possible because of the different amounts of hydrogen absorbed. For example, with 50 mg. of each catalyst, 1.342 g. (0.01 mol.) of cinnamyl alcohol was reduced in 11 min. with rhodium-platinum (3:1) oxide, in 14 min. with palladous oxide, and in 26 min. with platinum oxide, in 20 cc. of acetic acid at 25°C and under atmospheric pressure.

Catalytic Reduction of 3-Phenylpropargyl Alcohol and *cis*-Cinnamyl Alcohol.—Table IV summarizes the results of the hydrogenation of 3-phenylpropargyl alcohol and *cis*-cinnamyl alcohol in various solvents with the use of platinum oxide as a catalyst together with those of the trans isomer. It is seen from the table that 3-phenylpropargyl alcohol absorbs nearly one mole of hydrogen more than *cis*-cinnamyl alcohol in any solvent used. This means that little hydrogenolysis or none occurred before the reduction of the triple bond to the double bond. The result may be explained by the strong affinity of the triple bond for the catalyst surface, which may prevent the C–O linkage from being adsorbed

TABLE IV. CATALYTIC REDUCTIONS OF 3-PHENYLPROPARGYL ALCOHOL AND CINNAMYL ALCOHOL[a]

Solvent	Hydrogen uptake mol./mol.		
	3-Phenylpropargyl alcohol	Cinnamyl alcohol *cis*-	*trans*-
EtOH, 20 cc.	2.01	1.04	1.03
AcOH, 20 cc.	2.29	1.24	1.31
EtOH, 20 cc. + 3N HCl, 0.1 cc.	2.64	1.64	1.60
AcOH, 20 cc. + 3N HCl, 0.1 cc.	2.79	1.77	1.79

a) 0.01 mol. of the substrate was hydrogenated with 50 mg. of platinum oxide each time.

19) For the superacidic character of hydrochloric acid in acetic acid, see for instance; G. Schwarzenbach and P. Stensby, *Helv. Chim. Acta*, **42**, 2342 (1959).

20) This does not mean that the hydrogenation of the double bond is unaffected by acid, but does mean that the hydrogenolysis is much more promoted by acid than the hydrogenation.

21) This does not mean necessarily that platinum oxide has the highest activity for the hydrogenolysis. The lower values for palladous oxide may probably result from its greater activity for the hydrogenation of the double bond.

on the surface of the catalyst, just as the triple bond is more tightly adsorbed than the double bond. Though the fact that *cis*-cinnamyl alcohol absorbed almost as much hydrogen as its trans isomer seems to suggest isomerization to a large extent in the course of the reduction, it will be difficult to say whether or not this is the case from the data now available[22].

Summary

1. The hydrogenation and hydrogenolysis of cinnamyl alcohol was studied with platinum, palladium, rhodium, and rhodium-platinum catalysts. The following results were obtained:

(i) The absorption of hydrogen increases with respect to the solvents in the following order; ethanol, acetic acid, ethanol with hydrochloric acid, and acetic acid with hydrochloric acid. The order was interpreted as that of the abilities of the solvents as proton donors.

(ii) With respect to the catalysts, platinum oxide causes the maximum absorption of hydrogen, and rhodium added to platinum decreases the hydrogenolysis markedly.

(iii) With respect to the activities of the three oxide catalysts in acetic acid, the order was; rhodium-platinum (3 : 1) oxide > palladous oxide > platinum oxide.

2. From the comparison of the hydrogen uptakes by 3-phenylpropargyl alcohol and by *cis*-cinnamyl alcohol, it was shown that little hydrogenolysis or none occurs before the reduction of the triple bond of the phenylpropargyl alcohol to the double bond.

The authors wish to express their hearty thanks to Professor Yoshiyuki Urushibara for his valuable suggestions and encouragement. The authors are also indebted to the Ministry of Education for a Grant-in-Aid for Scientific Research.

Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo

22) Cf. R. L. Burwell, Jr., *Chem. Revs.*, **57**, 895 (1957).

Infrared Spectra and Normal Vibrations of Formamide; $HCONH_2$, $HCOND_2$, $DCONH_2$ and $DCOND_2$

By Isao SUZUKI

(Received May 7, 1960)

A number of investigations have been made on the molecular structure of formamide. The geometrical structure of the molecule was precisely determined by the studies of the microwave spectrum[1-3], X-ray diffraction[4], and nuclear magnetic resonance[5]. It was indicated that the formamide molecule is planar in the solid state and is nearly planar and of very shallow pyramidal configuration as to the C-NH_2 group in the gaseous state. The Raman and infrared spectra of $HCONH_2$ were observed by a number of investigators in the gaseous, liquid, and solid states and in solutions[6-13]. The infrared spectra of *N*-deuterated formamide, $HCOND_2$, were also observed in the liquid state and in solutions[11,13]. A normal coordinate treatment of the molecule as a three-body problem was made by Miyazawa[13]. However, a full analysis of the normal vibrations of the formamide molecule has never been attempted, and the assignments of the observed frequencies are not yet complete.

In order to clarify the nature of the normal vibrations of the formamide molecule, the present writer observed the infrared spectra of *C*-deuterated formamides; $DCONH_2$ and $DCOND_2$. The infrared spectra of undeuterated

1) R. J. Kurland, *J. Chem. Phys.*, **23**, 2202 (1955).
2) R. J. Kurland and E. B. Wilson Jr., ibid., **27**, 585 (1957).
3) C. C. Costain and J. M. Dowling, ibid., **32**, 158 (1960).
4) C. Post and J. Ladell, *Acta Cryst.*, **7**, 559 (1954).
5) R. A. Krombrout and G. B. Moulton, *J. Chem. Phys.*, **25**, 35 (1956).
6) B. D. Saksena, *Proc. Indian Acad. Sci.*, **11**, 53 (1940).
7) A. L. SunderRao, *J. Indian Chem. Soc.*, **18**, 337 (1941).
8) L. Kohovec and H. Wasmuth, *Z. Physik. Chem.*, **48B**, 70 (1941).
9) P. G. Puranik and K. Venkata Raman, *J. Mol. Spectroscopy*, **3**, 486 (1959).
10) J. Lecomte and R. Freymann, *Bull. Soc. Chim.*, **8**, 612 (1941).
11) J. C. Evans, *J. Chem. Phys.*, **22**, 1228 (1954); **31**, 1435 (1959).
12) M. Davies and J. C. Evans, ibid., **20**, 342 (1952).
13) T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **76**, 821 (1955); **77**, 366 (1956).

formamide ($HCONH_2$) and *N*-deuterated formamide ($HCOND_2$) have been remeasured.

A normal coordinate treatment has been made for all of these four molecules as a six-body problem. Fourteen force constants have been determined so that all the thirty-six observed frequencies are thereby explained. With these force constants, the vibrational mode and the potential energy distribution among the symmetry coordinates have been calculated for each normal vibration.

The purpose of this paper is to give the results of these observations and calculations and to present a complete assignment of the observed frequencies and a detailed discussion on the nature of each normal vibration of the formamide molecule.

Experimental

Formamide $HCONH_2$. — The sample used was obtained from a commercial source, and was purified several times by vacuum distillation; b. p. 86°C (5 mmHg).

***C*-Deuterated Formamide $DCONH_2$.**—This compound was prepared from DCOOD and urea by the following procedures. First, DCOOD was prepared by the thermal decomposition of anhidrous heavy oxalic acid $(COOD)_2$ which was obtained by the exchange reaction of $(COOH)_2$ and D_2O[14]. DCOOD was then mixed with urea and heated at about 150°C for 4 hr.[15] Ammonia, carbon dioxide and water produced by the reaction were pumped out in vacuum. From the residual, $DCONH_2$ was distilled out. It was treated with a small amount of aqueous solution of potassium hydroxide to neutralize the remaining free acid and distilled in vacuum again.

Replacement of the amide hydrogen by deuterium was accomplished by adding an excess of D_2O, evaporating the heavy water in vacuum, and repeating this procedure three times.

Infrared Spectra.—Infrared spectra were measured in the region from 3600 to 525 cm^{-1} with a Perkin-Elmer grating spectrometer model 112G equipped with a KBr foreprism[16], and in the region from 700 to 300 cm^{-1} with a Perkin-Elmer spectrometer model 21, equipped with a CsBr prism. All the measurements were made in the liquid state.

Infrared Spectra

Infrared spectra of $HCONH_2$ and $DCONH_2$ are shown in Figs. 1 (a)–(c), and those of $HCOND_2$ and $DCOND_2$ in Figs. 2 (a)–(c). As may be expected, the bands at 2882, 1391 and 1056 cm^{-1} of $HCONH_2$ which are assigned respectively to the CH stretching, CH in-plane and out-of-plane deformation vibrations, completely disappear on the *C*-deuteration, and

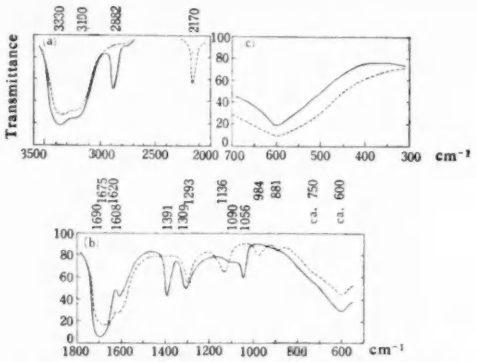


Fig. 1. Infrared spectra of $HCONH_2$ and $DCONH_2$.
(a) 3600~2000 cm^{-1} (b) 1800~525 cm^{-1}
(c) 700~300 cm^{-1};
—— $HCONH_2$ and ---- $DCONH_2$.

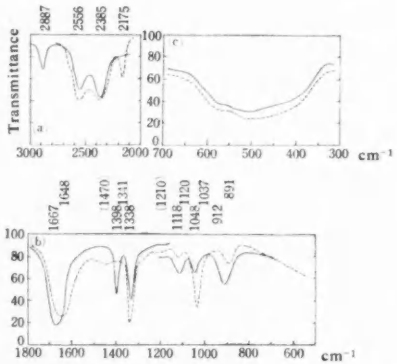


Fig. 2. Infrared spectra of $HCOND_2$ and $DCOND_2$.
(a) 3000~2000 cm^{-1} (b) 1800~525 cm^{-1}
(c) 700~300 cm^{-1};
—— $HCOND_2$ and ---- $DCOND_2$.

new bands appear at 2170, 984 and 881 cm^{-1}. These are assigned to the CD stretching, CD in-plane and out-of-plane deformation vibrations respectively. Besides these, every band below 1700 cm^{-1} is more or less affected by the *C*-deuteration as well as by the *N*-deuteration. This fact suggests that, in almost every normal mode, the CH, NH_2, CD and/or ND_2 deformation motions more or less take place.

When $HCOND_2$ or $DCOND_2$ was exposed in the atomopheric air for a while, several weak bands appeared besides the absorption bands illustrated in Figs. 2 (a)–(c). These bands are supposed to be arising from *N*-monosubstituted amides, which were produced by the partial hydrogenation due to the atomospheric water vapour. The positions of these bands were also determined; 3300, 2460, 1470, 1212 and about 700 cm^{-1} for HCONHD (both cis and

14) R. F. Curl, Jr., *J. Chem. Phys.*, **30**, 1529 (1959).
15) E. Cherabliez and F. Landolt, *Helv. Chim. Acta*, **29**, 1438 (1946).
16) S. Mizushima et al., A Report on the Perkin-Elmer Grating Spectrophotometer Model 112G, The Perkin-Elmer Corp. (1959).

TABLE I. THE SYMMETRY COORDINATES

Symmetry coordinate		Vibrational mode	Abr.
S_1	$(\Delta r_{NHa}-\Delta r_{NHb})/\sqrt{2}$	NH_2 antisym. stretching	$\nu_a(NH_2)$
S_2	$(\Delta r_{NHa}+\Delta r_{NHb})/\sqrt{2}$	NH_2 symm. stretching	$\nu_s(NH_2)$
S_3	Δr_{CH}	CH stretching	ν(CH)
S_4	Δr_{CO}	CO stretching	ν(CO)
S_5	Δr_{CN}	CN stretching	ν(CN)
S_6	$(2\Delta\alpha_{HNH}-\Delta\alpha_{CNHa}-\Delta\alpha_{CNHb})/\sqrt{6}$	NH_2 bending	b(NH_2)
S_7	$(\Delta\alpha_{NCH}-\Delta\alpha_{HCO})/\sqrt{2}$	CH deformation	δ(CH)
S_8	$(\Delta\alpha_{CNHa}-\Delta\alpha_{CNHb})/\sqrt{2}$	NH_2 rocking	r(NH_2)
S_9	$(2\Delta\alpha_{OCN}-\Delta\alpha_{NCH}-\Delta\alpha_{HCO})/\sqrt{6}$	NCO deformation	δ(NCO)
S_{10}	$(\Delta\alpha_{CNHa}+\Delta\alpha_{CNHb}+\Delta\alpha_{HNH})/\sqrt{3}$	redundant	—
S_{11}	$(\Delta\alpha_{NCH}+\Delta\alpha_{HCO}+\Delta\alpha_{OCN})/\sqrt{3}$	redundant	—

TABLE II. THE FINAL SET OF FORCE CONSTANTS (md/A)

K_{NH}	5.80	H_{HNH}	0.40	$F_{H\cdots H}$	0
K_{CH}	3.74	H_{HNC}	0.32	$F_{H\cdots C}$	0.46
K_{CO}	8.80	H_{HCN}	0.18	$F_{H\cdots N}$	0.70
K_{CN}	6.15	H_{HCO}	0.20	$F_{H\cdots O}$	0.92
$F'=-F/10$		H_{NCO}	0.34	$F_{O\cdots N}$	1.50

trans forms), and 3300, 2460, 1470, 1290, 1053 and about 700 cm^{-1} for DCONHD.

The values of the observed frequencies are given in the first column of Table III.

Calculation of Normal Vibrations

The calculation of normal vibrations was made by the method presented by Wilson[17], according to which the secular equation was set in the form $|\boldsymbol{GF}-\lambda\boldsymbol{E}|=0$, where $\boldsymbol{F}$ and $\boldsymbol{G}$ are the potential and reciprocal kinetic energy matrices respectively. It was assumed that the molecule has a planar configuration (C_s), the normal vibrations are classified into 9 in-plane (A′) and 3 out-of-plane (A″) vibrations. In the present paper, only the in-plane vibrations were treated. The structural parameters used in this calculation are as follows; the bond lengths of r(NH) = 1.04, r(CN) = 1.30, r(CH) = 1.07 and r(C=O) = 1.225 A[4,5], all the bond angles are assumed to be 120°. The symmetry coordinates $\boldsymbol{S}$ obtained from the internal coordinates $\boldsymbol{R}$ by a linear transformation;

$$\boldsymbol{S}=\boldsymbol{UR}$$

are given in Table I.

Force Constants. — The potential function employed in the calculation is of the Urey-Bradley type[18];

$$2V=\sum K_i(\Delta r_i)^2+\sum H_{ij}r^0{}_i r^0{}_j(\Delta\alpha_{ij})^2 + \sum F_{ij}(\Delta q_{ij})^2+\text{linear terms}$$

where r_i and r_j are bond lengths with equilibrium values $r^0{}_i$ and $r^0{}_j$; α_{ij} are bond angles and q_{ij} distances betweeen nonbonded atoms. K, H and F are stretching, bending and repulsive force constants respectively.

The values of the force constants were first transferred from diformylhydrazine, *N*-methylacetamide[19] and urea[20]. A refinement of the values of the force constants was made by the method developed by Miyazawa[21]. The final set of their values is given in Table II, and the calculated frequencies with these values are shown in the second column of Table III.

The calculated frequencies are in excellent agreement with the observed ones, the maximum deviation being 3.0% and the average deviation 1.3%. Therefore, the values of the force constants obtained in this calculation may be used for the normal vibration calculations of the molecules which are closely related with formamide[22].

***L* Matrix and Potential Energy Distribution.** — In order to clarify the nature of the observed frequencies precisely, it is desirable to calculate the relative amplitude of each symmetry coordinate in a given normal mode of vibration. The symmetry coordinates $\boldsymbol{S}$ are related linearly to the normal coordinates $\boldsymbol{Q}$ through the matrix expression;

$$\boldsymbol{S}=\boldsymbol{LQ}$$

The relative amplitude for each symmetry coordinate in a given normal vibration is given

17) E. B. Wilson, *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 96 (1941).
18) T. Shimanouchi, ibid., **17**, 245, 734, 848 (1949).
19) T. Miyazawa, T. Shimanouchi and S. Mizushima, ibid., **29**, 611 (1959).
20) A. Yamaguchi, T. Miyazawa, T. Shimanouchi and S. Mizushima, *Spectrochim. Acta*, **10**, 170 (1957).
21) T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **76**, 1132 (1955).
22) I. Suzuki, to be published.

TABLE III. THE OBSERVED AND CALCULATED FREQUENCIES, AND POTENTIAL ENERGY DISTRIBUTIONS

		Frequency			P. E. D. $(F_{ii}L^2_{is}/\lambda_s)\times 100$								
		ν_{obs}	ν_{calc}	Δ	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9
$HCONH_2$	ν_1	3330	3367	−1.1	100	0	0	0	0	0	0	0	0
	ν_2	3190	3268	−2.5	0	99	0	0	0	0	0	0	0
	ν_3	2882	2935	−1.8	0	0	102	0	0	0	0	0	0
	ν_4	1690	1681	+0.5	0	1	0	64	33	8	19	3	0
	ν_5	1608	1606	+0.1	0	0	0	11	3	85	3	1	1
	ν_6	1391	1398	−0.5	0	0	1	19	7	0	65	2	4
	ν_7	1309	1304	+0.4	0	0	0	1	57	6	13	13	9
	ν_8	1090	1103	−1.2	0	0	0	11	8	1	1	73	1
	ν_9	608	617	−1.5	0	0	1	0	0	0	0	8	90
$HCOND_2$	ν_1	2556	2494	+2.4	100	0	0	0	0	0	0	1	0
	ν_2	2385	2361	+1.0	0	98	0	0	2	1	0	0	0
	ν_3	2887	2936	−1.7	0	0	102	0	0	0	0	0	0
	ν_4	1667	1672	−0.3	0	0	0	73	29	1	22	2	0
	ν_5	1398	1400	−0.1	0	0	1	25	16	3	49	1	5
	ν_6	1338	1362	+1.8	0	2	0	1	43	22	30	1	3
	ν_7	1118	1098	+1.8	0	1	0	0	14	69	1	6	9
	ν_8	912	905	+0.8	0	0	0	6	4	4	0	66	13
	ν_9	570	554	+2.7	0	0	1	0	0	1	0	24	74
$DCONH_2$	ν_1	3330	3366	−1.1	100	0	0	0	0	0	0	0	0
	ν_2	3190	3266	−2.5	0	100	0	0	0	0	0	0	0
	ν_3	2170	2146	+1.1	0	0	103	2	1	0	0	0	1
	ν_4	1675	1669	+0.4	0	0	0	62	37	14	9	3	0
	ν_5	1620	1609	+1.2	0	1	0	18	1	80	2	1	1
	ν_6	1293	1313	−1.6	0	0	0	11	60	6	3	11	12
	ν_7	1136	1120	−1.4	0	0	0	13	2	0	8	71	2
	ν_8	984	998	−1.4	0	0	0	0	7	1	80	6	0
	ν_9	600	610	−1.5	0	0	0	0	0	0	1	8	90
$DCOND_2$	ν_1	2556	2498	+2.4	100	0	0	0	0	0	0	1	0
	ν_2	2383	2362	−0.9	0	98	0	0	2	1	0	0	0
	ν_3	2175	2146	+1.3	0	0	103	2	1	0	0	0	0
	ν_4	1648	1654	−0.4	0	0	0	78	32	1	11	2	0
	ν_5	1341	1366	−1.9	0	2	0	18	56	23	0	2	7
	ν_6	1120	1123	−0.3	0	1	0	2	8	63	19	1	6
	ν_7	1037	1006	+3.0	0	0	0	2	5	8	62	14	4
	ν_8	891	891	0	0	0	0	4	5	5	10	56	12
	ν_9	560	548	+2.4	0	0	0	0	0	0	1	24	76

$\Delta = [\nu_{obs} - \nu_{calc}/\nu_{obs}] \times 100$

by the corresponding element of the L matrix. The elements of the L matrix computed for each species of formamide are given in Table IV. (The L matrix is normalized to G; $LL' = G$[23])

It has been shown that the ratios of the potential energy distribution (P. E. D.) among the symmetry coordinates (S_i) for a given normal coordinate (Q_s) can approximately be expressed as $F_{ii}L^2_{is}/\lambda_s$,[24] where F_{ii} is a diagonal element of the F matrix, λ_s is sth frequency parameter. These are also computed and the results are shown in Table III.

Numerical Computations.—All the numerical computations were carried out with a parametron computor PC 1, which was designed and constructed by Professor H. Takahashi and his collaborators in the Department of Physics, Faculty of Science, University of Tokyo. The routines used in the computations have been programmed by Shimanouchi, Takeda and the present writer. The details will be published elsewhere[23].

The Nature of the Observed Bands

Based on the calculated values of vibrational amplitudes and potential energy distributions

23) T. Shimanouchi and I. Suzuki, to be published.
24) Y. Morino and K. Kuchitsu, *J. Chem. Phys.*, **20**, 1809 (1953). I. Nakagawa, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **74**, 243 (1953).

TABLE IV. THE ELEMENTS OF THE L MATRICES

	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	
Q_1	1.048	−0.001	−0.013	0.002	0.000	0.001	−0.051	0.128	0.076	
Q_2	0.001	1.012	−0.028	−0.002	−0.049	−0.196	−0.009	−0.001	−0.005	
Q_3	0.013	0.028	1.035	−0.031	−0.031	0.010	−0.031	0.075	0.114	
Q_4	0.003	0.007	−0.001	−0.316	0.254	0.530	−0.724	0.297	0.079	
Q_5	−0.002	0.053	−0.017	0.126	0.069	1.606	0.284	−0.158	−0.090	$HCONH_2$
Q_6	0.008	0.007	0.043	−0.142	−0.094	0.094	1.106	0.185	0.208	
Q_7	−0.004	−0.015	−0.018	0.033	0.258	−0.359	0.466	−0.453	−0.288	
Q_8	0.014	−0.002	−0.015	0.087	0.081	−0.097	0.129	0.914	0.105	
Q_9	−0.009	0.001	0.017	0.004	0.010	−0.028	−0.037	−0.170	0.427	
Q_1	0.776	−0.007	0.013	−0.002	0.001	0.004	−0.088	0.204	0.115	
Q_2	0.008	0.726	0.022	−0.001	−0.090	−0.250	−0.008	0.004	0.009	
Q_3	−0.010	−0.014	1.035	−0.031	−0.028	0.016	−0.029	0.067	0.112	
Q_4	0.007	−0.014	−0.003	0.336	−0.237	−0.149	0.770	−0.238	−0.082	
Q_5	0.008	−0.019	0.048	−0.165	−0.146	−0.272	0.959	0.148	0.239	$HCOND_2$
Q_6	0.009	0.052	−0.013	0.039	0.234	0.699	0.725	−0.156	−0.170	
Q_7	−0.006	0.035	0.011	−0.011	−0.106	0.992	−0.122	0.249	0.237	
Q_8	−0.003	−0.002	−0.003	0.053	0.046	−0.205	0.060	0.708	0.237	
Q_9	−0.011	0.001	0.015	−0.001	0.008	−0.044	−0.036	−0.261	0.347	
Q_1	1.048	−0.003	−0.003	0.001	0.000	0.001	−0.047	0.128	0.077	
Q_2	0.004	1.012	−0.006	−0.002	−0.050	−0.196	−0.007	0.000	−0.003	
Q_3	0.005	0.008	0.770	−0.064	−0.047	0.018	−0.035	0.145	0.184	
Q_4	0.004	0.012	−0.028	−0.310	0.266	0.680	−0.486	0.274	0.065	
Q_5	−0.003	0.052	0.003	0.162	0.038	1.553	0.198	−0.176	−0.091	$DCONH_2$
Q_6	0.006	0.017	−0.004	−0.101	−0.268	0.351	0.228	0.423	0.328	
Q_7	0.013	−0.001	−0.024	0.095	0.043	−0.053	−0.316	0.912	0.107	
Q_8	0.006	−0.001	0.009	0.003	0.067	−0.087	0.876	0.239	0.051	
Q_9	−0.009	0.001	0.011	0.003	0.009	−0.026	−0.056	−0.166	0.423	
Q_1	0.777	−0.004	−0.006	−0.001	0.001	0.004	−0.073	0.202	0.112	
Q_2	0.004	0.726	−0.028	0.003	−0.088	−0.251	0.004	−0.004	−0.001	
Q_3	0.006	0.027	0.760	−0.064	−0.051	−0.002	−0.033	0.126	0.183	
Q_4	0.004	−0.017	0.023	0.344	−0.245	−0.165	0.525	−0.231	−0.077	
Q_5	0.001	0.052	−0.001	0.135	0.268	0.711	−0.104	−0.194	−0.261	$DCOND_2$
Q_6	0.001	0.038	0.004	−0.041	−0.081	0.965	0.478	0.124	0.202	
Q_7	0.009	−0.007	0.018	−0.035	0.056	−0.307	0.773	−0.371	−0.143	
Q_8	−0.002	−0.002	−0.004	0.043	0.052	−0.226	0.282	0.643	0.226	
Q_9	−0.010	0.001	0.011	−0.001	0.007	−0.042	−0.056	−0.257	0.347	

shown in Tables III and IV, the nature of the observed bands will be discussed.

The Bands above 2000 cm^{-1}.—The 3330, 3190 and 2882 cm^{-1} bands of $HCONH_2$ are undoubtedly assigned respectively to the NH_2 antisymmetric, NH_2 symmetric stretching and the CH stretching vibrations. As may be seen from Table III, each of the normal vibrations corresponding to these frequencies takes place along one of these symmetry coordinates, and practically no other vibrations are coupled with it. The bands at 3330, 3190 and 2170 cm^{-1} of $DCONH_2$ are likewise shown to be almost pure NH_2 antisymmetric, NH_2 symmetric stretching and CD stretching vibrations respectively. In a similar way, each of the three high frequencies of $HCOND_2$ and $DCOND_2$ is assigned to almost pure ND_2 antisymmetric, ND_2 symmetric, CH or CD stretching vibration.

The calculated frequencies of these NH_2, ND_2, CH and CD stretching vibrations are in agreement with the observed ones with the maximum deviation of 2.5%. In detail, however, there are systematic deviations found between the calculated and observed frequencies. Namely, the frequency difference $\Delta\nu = \nu_{obs} - \nu_{calc}$ is always negative for the NH_2 and CH stretching vibrations and always positive for the ND_2 and CD stretching vibrations. This may be interpreted as due to the anharmonicity in the internal potential in which the hydrogen or deuterium atoms are placed, which is neglected in the present calculation.

The Band at 1690 cm^{-1}.—To this band there

are considerable contributions of both the ν(C=O) and ν(CN) vibrations. The energy associated with the ν(C=O) vibration is 50% of the total and that associated with the ν(CN) is 25%, while the amplitude ratio of the ν(CN) to the ν(C=O) is computed to be −0.73. Therefore, this band may well be called "N-C=O antisymmetric vibration" rather than "C=O stretching vibration". In addition, the contribution of the δ(CH) motion to this band is not negligible as it is in the case of *N*-methylformamide[22] and diformylhydrazine[19].

This band at 1690 cm^{-1} shifts towards lower frequency both on *N*-deuteration and *C*-deuteration the amount of shift being 23 and 15 cm^{-1} respectively. For $DCOND_2$, it is found at 1648 cm^{-1}. On the *C*-deuteration the contribution of the δ(CH) vibration is removed, and on the *N*-deuteration the interaction from the b(NH_2) vibration is removed. This may be the cause of the shifts of the band in question. The way of coupling of the ν(C=O) and ν(CN) vibrations in this normal mode seems to be unaffected by any deuteration.

The Band at 1608 cm^{-1}.—The band at 1608 cm^{-1} of $HCONH_2$ corresponds to almost pure b(NH_2) vibration. This band is not sensitive to the *C*-deuteration and is found at 1620 cm^{-1} in $DCONH_2$. The band corresponding to the b(ND_2) vibration is found at 1118 cm^{-1} in $HCOND_2$. The position of the band is hardly affected by *C*-deuteration, but its intensity becomes weaker.

The Band at 1391 cm^{-1}.—The band at 1391 cm^{-1} of $HCONH_2$ can be assigned to the δ(CH) vibration. However, contributions of both the ν(CN) and ν(C=O) vibrations are not negligible. In the normal vibration, the C-N and C=O bonds stretch and contract in phase with an amplitude ratio of +0.66. This band is not sensitive to *N*-deuteration and is found at 1398 cm^{-1} in $HCOND_2$. The band at 984 cm^{-1} in $DCONH_2$ corresponds to almost pure δ(CD) vibration. It shifts towards higher frequency on *N*-deuteration by 53 cm^{-1}. As is seen from Tables III and IV the shift can be explained as due to the interaction between δ(CD) and r(ND_2) vibrations.

The Band at 1309 cm^{-1}.—This band is mainly due to the ν(CN) vibration, although there are energetically small contributions of δ(CH) and r(NH_2) vibrations. The contribution of the ν(C=O) motion is shown to be quite negligible by the present calculation, in contradiction to some previous authors' expectation[12,13]. On *N*-deuteration the band moves to higher frequency by 29 cm^{-1}. The nature of the normal mode corresponding to this band is more complex. Here, the contributions of the δ(CH) and b(ND_2) vibrations are as important as the ν(CN) vibration.

It is noted that the contribution of the ν(C=O) vibration increases on *C*-deuteration, while that of the δ(CH) becomes negligible. In the corresponding normal vibration at 1341 cm^{-1} of $DCOND_2$ the energy associated with the ν(C=O) vibration is 16% of the total.

The Bands at 1090 and ca. 600 cm^{-1}.—The band which occurs at about 1090 cm^{-1} in $HCONH_2$ can be assigned to the r(NH_2) vibration, although there is a small contribution of the ν(C=O) vibration. On *C*-deuteration it shifts towards higher frequency by about 40 cm^{-1}. The broad band at about 600 cm^{-1} of $HCONH_2$ corresponds to almost pure δ(NCO) vibration. (It is overlapped with another broad band arising from the NH_2 wagging vibration.) The band is insensitive to *C*-deuteration. In *N*-deuterated formamides, an interaction between the r(ND_2) and δ(NCO) vibrations takes place, and this gives rise to two obserbed bands at 912 and about 570 cm^{-1} in $HCOND_2$ and those at 891 and about 560 cm^{-1} in $DCOND_2$. In addition, there is a small contribution of the δ(CD) vibration to the band at 891 cm^{-1} of $DCOND_2$.

The Out-of-plane Vibrations—Of three out-of-plane vibrations, two can easily be identified. They are the CH out-of-plane deformation and NH_2 wagging vibrations; π(CH) and w(NH_2).

Of $HCONH_2$, the π(CH) vibration is assigned to a band at 1056 cm^{-1}. On *N*-deuteration it is a little shifted, while on *C*-deuteration it disappears as is expected from the assignment. The band at 881 cm^{-1} in $DCONH_2$ can be assigned to the π(CD) vibration, although its intensity is comparatively weak. In $DCOND_2$ it is probably overlapped by the r(ND_2) band at 891 cm^{-1} and cannot be distinguished. The above assignment is consistent with the result given by a study on the infrared spectra of $DCONHCH_3$ and $DCONDCH_3$[22]. Both of them show a band at 864 cm^{-1}, the intensity of which is as weak as that of the 881 cm^{-1} band of $DCONH_2$.

A broad band found at about 750 cm^{-1} in both $HCONH_2$ and $DCONH_2$ is assigned to the w(NH_2) vibration. On *N*-deuteration it moves to lower frequency up to about 450 cm^{-1}.

Another out-of-plane vibration, the NH_2 twisting or torsional vibration, is expected to occur at a lower frequency than 300 cm^{-1}. The Raman line found at 200 cm^{-1} of $HCONH_2$[9] may be assigned to this vibration.

Thus, a complete assignment has been made of the infrared absorption bands of the four isotopic species of formamide observed in the 3600~300 cm^{-1} region. The present assignment for $HCONH_2$ and $HCOND_2$ is in comformity

with that proposed by Miyazawa[13] except for a few minor points, but considerably different from others' assignments.

The present writer wishes to express his gratitude to Professor Takehiko Shimanouchi for his kind guidance and encouragement throughout this work and to Professor Hidetoshi Takahashi for allowing to use the PC-1 computor. His thanks are also due to Dr. Michiro Kawano for the infrared measurements in the CsBr region.

Department of Chemistry
Faculty of Science
University of Tokyo
Hongo, Tokyo

Investigation on Mixed Complexes. V. A Conductometric Study of Cyano-ethylenediamine Complexes

By Sigeo KIDA

(Received February 15, 1960)

In the preceding papers of this series[1-3], the present author has dealt with the formation of mixed cyano complexes in solution. It was indicated spectrophotometrically that the octahedral nickel(II) complex ion, such as the hexaquo nickel(II) ion or the bis-(ethylenediamine)-nickel(II) ion, does not react with planar nickel(II) complexes, for example tetracyano niccolate(II) or bis-(dithio-oxalato)-niccolate(II) ion, to form a mixed complex. However, nickel(II) complexes have a tendency to react with each other, when they are of similar configuration, to produce mixed complexes as shown in the following expression:

$$[Ni(C_2S_2O_2)]^{2-} + [Ni(CN)_4]^{2-} \rightleftarrows 2[Ni(C_2S_2O_2)(CN)_2]^{2-}$$

where $C_2S_2O_2$ indicates dithio-oxalate. However, in the case of platinum(II) complex ions such as tetrachloro platinate(II), tetrabromo platinate(II) and tetracyano platinate(II) ions, all of which are of similar configuration, no tendency of forming any mixed cyano-halogeno complex has been observed in solution.

In order to ascertain the exact conditions under which a cyano mixed complex is formed, one needs to carry out further experiments, but unfortunately it is not always easy to find substances which are suitable for the examination by spectrophotometric methods as previously reported. In the present investigation therefore, the conductometric method has been applied to the complexes of platinum(II), palladium(II), zinc(II) and cadmium(II), which are all colorless and hence can not be studied by the spectrophotometric method[4].

Results and Discussion

It is known that the conductivity of a solution has no linear relationship to the concentration of the dissolved salt in the range of 10^{-2} F, used in the present study. A linear relationship, however, is required by the method of continuous variation[5]. However, the data reported in the present work show that, so far as only the detection of a mixed complex formation is desired, the conductometric continuous variation method can be applied satisfactory for this purpose.

Eight solutions were prepared for the respective metals by mixing a solution of the ethylenediamine complex with the potassium cyanide solution in the ratios as shown in Table I. The conductivity was measured at 25°C.

Table I. Composition of mixed solutions used in the conductometric measurements

0.01 F $[M\,en_n]X_2$	20	10	10	10	10	10	5	5 ml.
0.02 F KCN	10	7.5	10	12.5	15	20	12.5	15
[CN]/[M]	1	1.5	2	2.5	3	4	5	6

X=Cl, NO_3, $1/2(SO_4)$

1) Part IV of this series: S. Kida, This Bulletin, 33, 1204 (1960).
2) S. Kida, ibid., 33, 587 (1960).
3) S. Kida, ibid., 32, 981 (1959).

4) The absorption of these complexes in the ultraviolet region are irregular and complicated, probably owing to the presence of association bands resulting from the complex and simple ions in the solution.
5) R. C. Brasted and W. E. Cooley, "Physical Methods in Coordination Chemistry", Ch. 18 in J. C. Bailar and D. H. Busch, ed., "The Chemistry of the Coordination Compounds", Reinhold Pub. Co., New York, (1956), pp. 569-572 and references therein.

The reaction proceeds to decrease the total ionic charge in the solution as follows:

$$[M\,en_n]^{2+} + 4CN^- \rightarrow [M(CN)_4]^{2-} + n\,en \quad (1)$$

or $[M\,en_n]^{2+} + 2CN^-$

$$\rightarrow [M\,en(CN)_2] + (n-1)en \quad (2)$$

(M=Ni, Pd, Pt, Zn and Cd; $n=2$ for Pd and Pt; $n=3$ for Ni, Zn and Cd).

Therefore, if a reaction of type 1 took place in solution the curves in Figs. 1 and 2 should have minimum points at [M]/[CN]=1:4, while that of type 2 should give a minimum point at [M]/[CN]=1:2. In fact, as can be seen in Figs. 1 and 2, minimum points are found at [M]/[CN]=1:4 on curves A and E, and at [M]/[CN]=1:2 on curves B, C and D. This shows that, in the former cases, mixed complexes, such as $[Ni\,en(CN)_2]$ and $[Pt\,en(CN)_2]$, are not formed, but the following reactions take place:

$$[Ni\,en_3]^{2+} + 4CN^- \rightarrow [Ni(CN)_4]^{2-} + 3\,en$$

and

$$[Pt\,en_2]^{2+} + 4CN^- \rightarrow [Pt(CN)_4]^{2-} + 2\,en$$

while in the latter cases the mixed complexes

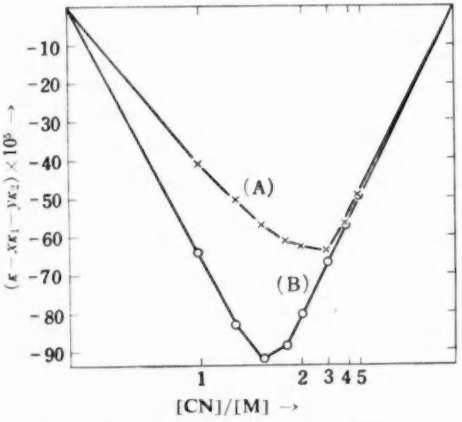


Fig. 1. The curves, (A) and (B), are referred to the complexes of Pd(II) and Pt(II), respectively.
[M]=Concentration of metal in F.
[CN]=Concentration of cyanide ion in F.
κ=Specific conductivity of a mixed solution ($\Omega^{-1}\times cm^{-1}$).
κ_1=Specific conductivity of a 0.01 F $[M\,en_n]X_2$ solution ($\Omega^{-1}\times cm^{-1}$).
κ_2=Specific conductivity of a 0.02 F KCN solution ($\Omega^{-1}\times cm^{-1}$).
x=Volume of the complex solution/Volume of the mixed solution.
y=Volume of the cyanide solution/Volume of the mixed solution.

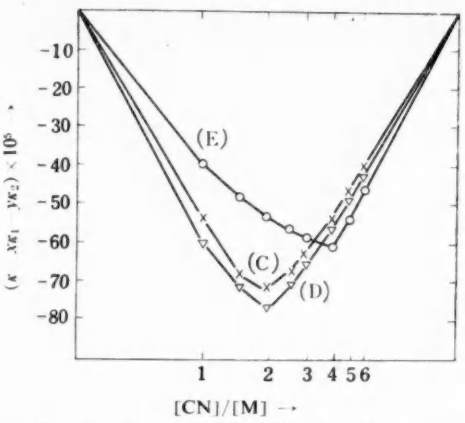


Fig. 2. Curves, (C), (D) and (E), are referred to the complexes of Zn(II), Cd (II) and Ni(II), respectively.

of zinc(II), cadmium(II) and palladium(II) were formed in the solutions through the following reactions:

$$[Zn\,en_3]^{2+} + 2CN^- \rightarrow [Zn\,en(CN)_2] + 2\,en^{6)}$$
$$[Cd\,en_3]^{2+} + 2CN^- \rightarrow [Cd\,en(CN)_2] + 2\,en^{6)}$$
$$[Pd\,en_2]^{2+} + 2CN^- \rightarrow [Pd\,en(CN)_2] + en$$

The result obtained for the nickel complex is in accord with that in the spectrophotometric investigation[3], showing that this conductometric method can be used for the purpose above mentioned. In the cases of zinc, cadmium and palladium complexes, minimum points are found only at [M]/[CN]=1:2 and not at [M]/[CN]=1:4. Neverthless, it should be noted that the formation of tetracyano complexes can not be neglected, since the reaction, $[M\,en(CN)_2] + 2CN^- \rightarrow [M(CN)_4]^{2-} + en$, does not give rise to any decrease in ionic charge in the solution, and accordingly the formation of dicyano complex succeeded by that of tetracyano complex does not always give a minimum point at [M]/[CN]=1:4.

It should also be noted that the curve of the platinum complex is in sharp contrast to that of palladium as a result of their different behavior; the formation of mixed cyano complexes was verified in all the cases of the other metallic ions, but no mixed cyano complex of platinum(II) has ever been observed.

6) It is known that $[Zn\,en_3]^{2+}$ and $[Cd\,en_3]^{2+}$ have octahedral configuration, while $[Zn(CN)_4]^{2-}$ and $[Cd(CN)_4]^{2-}$ are tetrahedral in configuration. However, J. Bjerrum (*Chem. Revs.*, **46**, 381 (1950)) has pointed out that tetrammine or bis-ethylenediamine zinc(II) and cadmium(II) complexes tend to be four-co-ordinated and have a tetrahedral configuration as in $[Zn\,en_2]^{2+}$ and $[Cd\,en_2]^{2+}$, but do not tend to have an octahedral one as in $[Zn\,en_2(OH_2)_2]^{2+}$ or $[Cd\,en_2(OH_2)_2]^{2+}$. Therefore, the mixed complexes present in the solution may possibly have tetrahedral configurations of the formulae, $[Cd\,en(CN)_2]$ and $[Zn\,en(CN)_2]$.

The cause of this fact will be the subject of the next investigation.

Experimental

Conductometric Measurement.—The conductivities of the solutions were measured at 25°±0.1°C with Kohlrausch's bridge. The cell constant was determined by using a standard potassium chloride solution of 0.01 F. In the cases of platinum(II) and palladium(II) complexes, the substitution reaction of the cyanide ion for the ethylenediamine molecule was slow, and accordingly the mixed solution was allowed to stand in a thermostat until the conductivity came to show a constant value in each case.

Materials. — $[Pt\,en_2]Cl_2$[7], $[Ni\,en_3](NO_3)_2$[8], $[Zn\,en_3]SO_4$[9] and $[Cd\,en_3]Cl_2$[10] were prepared according to the methods described in the references. $[Pd\,en_2]Cl_2$[11] was prepared in a way similar to that for $[Pt\,en_2]Cl_2$. The purity was checked by determining the chloride with silver nitrate.

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Summary

The conductometric method was applied to the determination of the formation of mixed complexes in solution, using the method of continuous variation. It was shown that

1) $[Ni\,en_3]^{2+}$ reacts with CN^- and forms $[Ni(CN)_4]^{2-}$ only, leading to the same conclusion as in the spectrophotometric investigation carried out previously.

2) $[Pt\,en_2]^{2+}$ forms only a tetracyano complex, but no mixed dicyano complex.

3) $[Pd\,en_2]^{2+}$, $[Zn\,en_3]^{2+}$ and $[Cd\,en_3]^{2+}$ form dicyano-ethylenediamine complexes in solution.

The author wishes to express his sincere thanks to Professor R. Tsuchida of Osaka University for his kind advice and encouragement during this work. His appreciation is also expressed to Dr. H. Yoneda for his helpful discussion.

Department of Chemistry
Wakayama University
Masagocho, Wakayama

2-Carboxymethylthio- and 2-Hydrazino-1, 3-diazaazulenes

By Ichiro MURATA

(Received March 1, 1960)

2-Mercapto-1, 3-diazaazulene[1] (I) easily undergoes condensation with monochloroacetic acid to form 2-carboxymethylthio-1, 3-diazaazulene[2] (II), as has already been reported, and various properties of II, and 2-hydrazino-1, 3-diazaazulene[3] derived from I and II, are described in this paper.

II forms a pale yellow, crystalline powder only sparingly soluble in water and organic solvents, and has a melting point exceeding 300°C. Its esterification by the Fischer method affords methyl ester IV of m. p. 118~118.5°C and the ethyl ester V of m. p. 89°C. V is also obtained upon reaction of ethyl monochloroacetate on the sodium salt of I. These esters easily undergo hydrolysis to regenerate II and are converted into an amide (VI) of m. p. 207~208°C by the action of 40% ammonia water.

It is known, that pyridines[4] and quinolines[5] possessing a carboxymethylthio group in the α-position generally form a cyclized product, called meso-ionic compound, on heating with acetic anhydride. On refluxing II in acetic anhydride, it is converted into an extremely sparingly soluble substance* of violet color. The analytical values of this substance suggest an intermolecular dehydrated product but no detailed examination has been made on it.

* A part of this work was presented as a paper at the 10th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1957.
1) T. Nozoe, T. Mukai and I. Murata, *J. Am. Chem. Soc.*, **76**, 3352 (1954).
2) I. Murata, This Bulletin, **33**, 56 (1960).
3) T. Nozoe, T. Mukai and I. Murata, *Proc. Japan Acad.*, **30**, 482 (1954).

4) E. Koenigs and H. Geisler, *Ber.*, **57**, 2076 (1924); G. F. Duffin and J. D. Kendall, *J. Chem. Soc.*, **1951**, 734.
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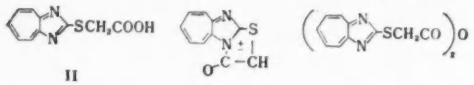
* Duffin and Kendall[4] reported that the use of phosphorus pentoxide or thionyl chloride in place of acetic anhydride as the dehydration agent afforded structurally unkonwn substance as a brown powder.

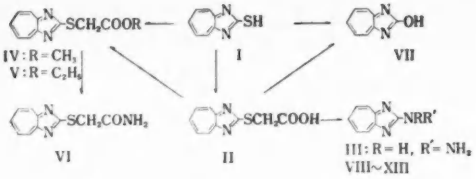


II

Refluxing of II in concentrated hydrochloric acid results in its conversion to 2-hydroxy-1, 3-diazaazulene (VII) in good yield. Such comparatively facile hydrolysis of II suggests the possibility of I being desulfurized by the action of monochloroacetic acid.

Desulfurization of heterocyclic compounds with a mercapto group by the action of monochloroacetic acid has been reported by numerous workers on thiopyrimidines[6], thioquinoline[7], thiohydantoin[8], thiouracil[9] and thiooxazole and thiothiazole[10]. On heating I in aqueous solution of excess of monochloroacetic acid, II is first formed after 15~20 min. When this mixture is heated for a longer period, such as further 25 hr., without isolation of II, the separated II dissolves gradually and changes almost quantitatively into VII.

Oxidation of the ethyl ester V with hydrogen peroxide in glacial acetic acid, in an attempt to obtain the ethoxycarbonylsulfonyl derivative, invariably gives VII as the product, whether the reaction is carried out at 60~70°C with an excess of the reagent or at room temperature with an equivalent amount of the reagent, and the sulfone is not isolated. Ohta[10] obtained the sulfone by oxidation of carboxymethylthio derivatives of thiazole and thiadiazole under the same conditions but found that the same oxidation of oxadiazole had changed it into the hydroxy derivatives and the sulfone was not obtained. II also undergoes oxidation by hydrogen peroxide to form VII.



The carboxymethylthio group present in 2-position of pyrimidine is known to be substituted by amino and benzylamino groups[11]. II also reacts comparatively easily with various amines to form derivatives listed in Table I.

In the foregoing reaction, II reacts most readily with hydrazine and III is formed in a good yield only by letting stand their mixture at room temperature.

III has already been obtained by the application of hydrazine to 2-chloro-1, 3-diazaazulene but its properties are almost unknown. As has already been mentioned, III can now be prepared easily from II but it can also be obtained easily from I by refluxing it with hydrazine hydrate in butanol, generating hydrogen sulfide gas.

III easily undergoes condensation with various ketones and aldehydes in alcohol to form the corresponding hydrazones (Table II). The ultraviolet absorption maxima of these hydrazones are indicated in Table III.

In general, six-membered, heterocyclic aromatic compounds of nitrogen possessing a hydrazino group in the α-position undergoes cyclization between the ring nitrogen and the hydrazino group by the action of formic acid, ethyl orthoformate, or acetic anhydride and form triazole derivatives. They also undergo

TABLE I. 2-SUBSTITUTED DERIVATIVES OBTAINED FROM 2-CARBOXYMETHYLTHIO COMPOUND

Compd. No.	R	R'	Cryst. form*	m. p., °C	Yield %	N Analysis Calcd.	N Analysis Found	Ref.
III	H	NH_2	y. N.	189	89	—	—	3
VIII	H	H	y. N.	295(d.)	43	—	—	12
IX	H	CH_3	y. P.	172~173	90	—	—	3
X	CH_3	CH_3	y. P.	133~134	92	—	—	3
XI	H	C_6H_5	o. P.	239~240	80	—	—	2
XII	H	$CH_2C_6H_5$	y. P.	173	75	17.86	17.92	—
XIII	H	NHC_6H_5	y. P.	222	30	23.72	23.40	—

* y, yellow; o, orange; N, needles; P, prisms.

6) T. B. Johnson and A. W. Joyce, *J. Am. Chem. Soc.*, **38**, 1385 (1916); A. R. Todd, *J. Chem. Soc.*, **1946**, 357; D. J. Brown, *J. Soc. Chem. Ind. (London)*, **69**, 353 (1950).
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Table II. Reaction products of III with various ketones and aldehydes

R_1	R_2	Cryst. form*	m.p. °C	Mol. form	Analysis Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
CH_3	CH_3	y. N.	201(d.)	$C_{11}H_{12}N_4$	65.98	6.04	27.98	67.05	5.72	27.67
H	C_6H_5	y. N.	235(d.)	$C_{15}H_{12}N_4$	72.56	4.89	22.57	72.51	4.59	22.56
H	C_6H_4Br	y. N.	274(d.)	$C_{15}H_{11}N_4Br$	55.06	3.38	17.12	55.63	3.48	17.11
H	$C_6H_4N(CH_3)_2$	r. P.	247(d.)	$C_{17}H_{17}N_5 \cdot H_2O$	66.00	6.19	22.64	66.18	6.21	22.81
H	$C_6H_4OCH_3$	o. P.	241(d.)	$C_{16}H_{14}ON_4 \cdot 1/2H_2O$	66.88	5.26	19.50	66.80	4.78	19.52
H	$C_6H_4NO_2$	y. N.	290	$C_{15}H_{11}O_2N_5 \cdot 3/2H_2O$	56.24	4.45	21.86	55.87	4.39	21.86
H	$C_6H_4O_2CH_2$	o. P.	262(d.)	$C_{16}H_{12}O_2N_4 \cdot H_2O$	61.93	4.55	18.06	62.12	4.05	18.55

* y, yellow; r, red; o, orange; N, needles; P, prisms.

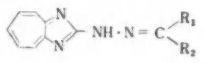


Table III. Ultraviolet maxima of 1,3-diazaazulenyl-2-hydrazones

R_1	R_2	λ_{max}^{MeOH} mμ (log ε)				
CH_3	CH_3	—	248(4.46)	264(4.46)	295(*)	370(4.35)
H	C_6H_5	—	243(4.46)	285(4.38)	305(*)	389(4.50)
H	C_6H_4Br-*p*	—	242(4.48)	286(4.37)	305(*)	391(4.55)
H	$C_6H_3O_2CH_2$-3,4	219(4.33)	245(4.46)	287(4.30)	312(4.22)	400(4.46)
H	$C_6H_4OCH_3$-*p*	—	245(4.46)	289(4.26)	310(4.21)	408(4.41)
H	$C_6H_4NO_2$-*p*	—	240(4.42)	268(*)	300(*)	410(4.57)
H	$C_6H_4N(CH_3)_2$-*p*	—	242(4.43)	265(*)	317(4.35)	428(4.47)

* shoulder

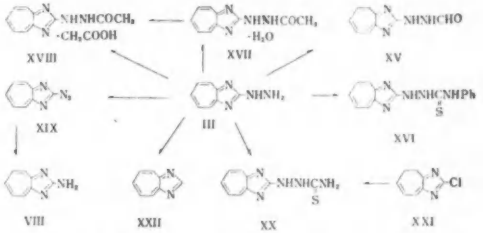
cyclization by the action of nitrous acid to form tetrazole derivatives[13].

III does not cyclize by the reaction of these reagents, even under a rather drastic conditions. The reaction of III with formic acid gives the formate XV of m. p. 249°C (decomp.) and that with phenyl-mustard oil gives the phenylthiosemicarbazide compound XVI. Application of acetic anhydride to III affords two kinds of crystals, m. p. 248°C (decomp.) (XVII) and m. p. 189°C (decomp.) (XVIII). Further application of acetic anhydride to XVII converts it to XVIII. It is therefore known that XVII is an acetylhydrazino compound with one molecule of water of crystallization while XVIII is an acetate of the acetylhydrazino compound.

Application of sodium nitrite in 2 N hydrochloric acid or in acetic acid to III gives extremely labile yellow needles (XIX) of m. p. 135°C (decomp.). The ultraviolet absorption maxima of XIX appear at 228 mμ (log ε 4.03), 262 (4.41), and 337 (4.15), and this makes it impossible to assume any skeletal change in 1,3-diazaazulene molecule. The infrared spectrum of XIX shows distinct absorption of an azide at 2150 cm^{-1} [14] and XIX should therefore be 2-azido-1,3-diazaazulene and not the anticipated tetrazole compound. Actually, reduction of XIX with hydrogen sulfide results in quantitative formation of 2-amino-1,3-diazaazulene[12] and this also endorses above assumption.

Reaction of potassium thiocyanate on III in the presence of hydrochloric acid affords reddish brown prisms XX, m. p. 179.5°C, which is also obtained upon reaction of thiosemicarbazide on 2-chloro-1,3-diazaazulene (XXI), and this shows that XX is 2-thiosemicarbazido-1,3-diazaazulene.

III was decomposed by the Stephens-McFadyen method[15] to 1,3-diazaazulene (XXII).



13) A. A. Morton, "The Chemistry of Heterocyclic Compounds", McGraw-Hill Book Company, Inc., New York (1946).

14) E. H. Eyster, *J. Chem. Phys.*, **8**, 369 (1940); E. Lieber, D. R. Levering and L. J. Patterson, *Anal. Chem.*, **23**, 1594 (1951).

15) H. E. Baumgarten and H. Chien-Fan Su, *J. Am. Chem. Soc.*, **74**, 3830 (1952).

Experimental

2-Carboxymethylthio-1, 3-diazaazulene (II).—Prepared by the method given in the literature[2].

2-Methoxycarbonylmethylthio-1, 3-diazaazulene (IV).—A mixture of II (100 mg.) suspended in methanol (2 ml.) and added with concentrated hydrochloric acid (0.05 ml.) was refluxed on a water bath for 45 min. This mixture was diluted with water and extracted with chloroform. The chloroform extract was washed with water, dried, and the solvent was evaporated. The residue was dissolved in benzene and the solution was purified by passage through an alumina layer. The yellow crystals (100 mg.), m. p. 120~122°C, was recrystallized from benzenepetroleum ether mixture to pale yellow needles (IV), m. p. 121~122°C.

Found: C, 56.71; H, 4.08; N, 12.12. Calcd. for $C_{11}H_{10}O_2N_2S$: C, 56.41; H, 4.30; N, 11.96%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 238(4.35), 269(4.28), 355(4.19).

2-Ethoxycarbonylmethylthio-1, 3-diazaazulene (V).—a) Obtained by a method similar to that for IV, as pale yellow needles, m. p. 89~89.5°C.

b) A solution of the sodium salt (200 mg.) of I dissolved in ethanol (2 ml.) and added with ethyl monochloroacetate (150 mg.) was refluxed on a water bath for 50 min. Sodium chloride formed by the reaction was filtered off, ethanol was evaporated from the filtrate and benzene soluble portion of the residue afforded 230 mg. of V, m. p. 89~89.5°C.

Found: C, 58.11; H, 4.39; N, 11.56. Calcd. for $C_{12}H_{12}O_2N_2S$: C, 58.06; H, 4.87; N, 11.29%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 238(4.46), 269(4.37), 355(4.29).

2-Carbamoylmethylthio-1, 3-diazaazulene (VI).—A mixture of V (70 mg.) and 40% ammonia water (2 ml.) was stirred for 10 hr. at room temperature. After allowing this to stand over night, the crystals (60 mg.) of m. p. 202~205°C (decomp.) were collected and recrystallized from ethanol to pale yellow needles (VI), m. p. 207~208°C (decomp.).

Found: C, 55.15; H, 3.82; N, 19.57. Calcd. for $C_{10}H_9ON_3S$: C, 54.79; H, 4.14; N, 19.17%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 239(4.49), 270(4.36), 355(4.29).

Action of Acetic Anhydride on II.—A suspension of II (40 mg.) in acetic anhydride (1 ml.) was refluxed for 10 min. in an oil bath. The cooled reaction mixture was thoroughly washed with water and ethanol, and brownish violet powder (30 mg.) which turns black from around 220°C, was obtained.

Found: N, 12.83. Calcd. for $C_{20}H_{14}O_3N_4S_2$: N, 12.54%.

Hydrolysis of II.—A solution of II (50 mg.) dissolved in concentrated hydrochloric acid (0.5 ml.) was refluxed for 2 hr. in an oil bath, hydrochloric acid was evaporated to dryness, and the residue was neutralized with sodium hydrogen carbonate, and crystals (30 mg.) melting at 225~228°C were obtained. Recrystallization from ethanol after treatment with activated carbon afforded crystals of m. p. 244~245°C, undepressed on admixture with VII.

Reaction of I and Monochloroacetic Acid.—a) A suspension of I (100 mg.) in a mixture of monochloroacetic acid (100 mg.) and water (10 ml.) was refluxed for 20 min. in an oil bath, cooled, and the crystals that separated out were collected by filtration to 80 mg. of II, m. p. over 300°C.

b) The reaction was carried out as above but the refluxing was continued for 25 hr. by which the crystals of II dissolved completely. The reaction mixture was evaporated to dryness, ethanol was added to the residue, and this was filtered. The crystals (100 mg.) of m. p. over 300°C so obtained were neutralized with sodium hydrogen carbonate and recrystallized from ethanol to VII, m. p. 244~245°C.

Oxidation of II with Hydrogen Peroxide.—To a suspension of II (80 mg.) in glacial acetic acid (0.5 ml.), 30% hydrogen peroxide (0.2 ml.) was added and the mixture was heated with stirring at 75~80°C for 2 hr. The pale yellow solution so obtained was concentrated under a reduced pressure and neutralized with saturated solution of sodium hydrogen carbonate. The crude crystals (40 mg.) of m. p. 229°C were recrystallized from ethanol to VII, m. p. 244~245°C.

Reaction of II and Ammonia or Amines.—a) A solution of II (100 mg.) dissolved in 40% ammonia water (1.5 ml.) was sealed in a tube and heated at 100°C for 6 hr. The reaction mixture was allowed to stand over night and the crystals (30 mg.) of m. p. 270°C (decomp.) were collected and recrystallized from water to pale yellow needles (VIII), m. p. 294°C (decomp.). The mother liquor left after separation of VIII afforded the recovered II (55 mg.).

b) A solution of II (150 mg.) dissolved in 40% aqueous solution (2 ml.) of methylamine or dimethylamine was sealed in a tube and heated at 100°C for 20 hr. The reaction mixture was evaporated to dryness over sulfuric acid in a vacuum desiccator and the benzene soluble portion of this residue afforded IX, m. p. 173~174°C, and X, m. p. 133~134°C.

c) A mixture of II (150 mg.) in ethanol (2 ml.) and aniline or benzylamine (1 ml.) was heated in a sealed tube at 165~170°C for 7 hr., cooled over night, and crystals that separated out were collected, afforded 120 mg. of XI, m. p. 239°C, and XII, m. p. 173°C.

2-Phenylhydrazino-1, 3-diazaazulene (VIII).—A mixture of II (100 mg.) in ethanol (4 ml.) and added with phenylhydrazine (100 mg.) was heated in a sealed tube at 155~160°C for 6 hr. The crystals that separated out on allowing the reaction mixture to cool were collected (30 mg.) melting with decomposition at 200°C. This was recrystallized from dilute ethanol to orange prisms, XIII, m. p. 222°C (decomp.).

Found: C, 70.64; H, 5.25; N, 23.40. Calcd. for $C_{14}H_{12}N_4$: C, 71.16; H, 5.12; N, 23.72%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 238(4.18), 260(4.56), 354(4.22).

2-Hydrazino-1, 3-diazaazulene (III).—a) II (1 g.) was dissolved in hydrazine hydrate (10 ml.) with warming and the solution was allowed to cool to room temperature by which brown needles, m. p.

187°C (decomp.), separated out. This was recrystallized from ethanol to III (650 mg.), m. p. 188~189°C (decomp.).

b) To a suspension of I (250 mg.) in *n*-butanol (6 ml.), 80% hydrazine hydrate (0.5 ml.) was added and the mixture was refluxed in an oil bath for 4 hr., until there was no longer evolution of hydrogen sulfide. The solvent was evaporated under a reduced pressure, ethanol was added to the residue, and filtration afforded III (220 mg.), m. p. 184~185°C (decomp.).

Reaction of III and Carbonyl Compounds.—A mixture of III and a carbonyl compound (1.1 mol. equiv.) in ethanol was heated for 5~10 min., cooled, and the crystals so formed or obtained by evaporation of ethanol was recrystallized from ethanol or a mixed solvent of ethanol and dioxane. The hydrazones listed in Table II were thereby obtained in a quantitative yield.

Reaction of III and Formic Acid.—A solution of III (100 mg.) dissolved in 80% formic acid (1 ml.) was heated at 90°C for 4 hr. Formic acid was then evaporated under a reduced pressure, the residue was washed with ethanol, and crystals (85 mg.) of m. p. 245°C (decomp.) were obtained. Recrystallization from ethanol afforded XV, m. p. 249°C (decomp.).

Found: C, 57.36; H, 3.90; N, 30.41. Calcd. for $C_9H_8ON_4$: C, 57.44; H, 4.29; N, 29.77%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 257(4.42), 347(4.09).

Reaction of III and Phenyl-mustard Oil.—Phenyl-mustard oil (90 mg.) was added to the solution of III (100 mg.) dissolved in ethanol (6 ml.) and the mixture was refluxed for 15 min. The crystals that separated out on cooling this reaction mixture were collected by filtration and recrystallized from ethanol to XVI (90 mg.) as reddish violet prisms, which does not indicate any definite melting point, gradually turning black by heating.

Found: C, 59.62; H, 4.00; N, 23.28. Calcd. for $C_{15}H_{13}N_5S$: C, 61.01; H, 4.44; N, 23.72%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 257(4.61), 347(4.13), 460 (3.50).

Reaction of III and Acetic Anhydride.—A mixture of III (50 mg.) and acetic anhydride (0.2 ml.) was allowed to stand at room temperature by which III dissolved once and crystals (30 mg.) of m. p. 210°C separated out. These crystals were recrystallized from ethanol to XVII, m. p. 248°C (decomp.).

Found: C, 54.38; H, 5.34; N, 25.22; H_2O, 7.72. Calcd. for $C_{10}H_{10}ON_4 \cdot H_2O$: C, 54.54; H, 5.49; N, 25.44; H_2O, 8.18%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 259(4.48), 350(4.18).

The filtrate left after separation of XVII was concentrated and the crystalline residue was recrystallized from ethanol to XVIII (10 mg.), m. p. 189°C (decomp.).

Found: C, 55.18; H, 5.10; N, 21.34. Calcd. for $C_{10}H_{10}ON_4 \cdot CH_3COOH$: C, 54.95; H, 5.38; N, 21.37%.

Reaction of III and Nitrous Acid.—A solution of sodium nitrite (95 mg.) in water (0.3 ml.) was added dropwise into a solution of III (200 mg.) dissolved in 2 N acetic acid (2 ml.) at room temperature. The mixture was then heated for a few minutes at 80°C, diluted with water, and extracted with benzene. The benzene layer was treated with activated carbon and crystals, m. p. 133~134°C (170 mg.), were obtained. This was recrystallized from benzene-petroleum ether mixture to pale yellow prisms XIX, m. p. 134~135°C (decomp.). Ultraviolet λ_{max}^{MeOH} mμ (log ε): 228(4.03), 262(4.41), 337(4.15), 370(shoulder).

Picrate: Yellow needles from ethanol, m. p. 273~274°C (decomp.).

Found: N, 15.68. Calcd. for $C_5H_5N_5 \cdot C_6H_3O_7N_3$: N, 15.79%.

Hydrogen sulfide gas was passed through a solution of XIX (100 mg.) dissolved in water (8 ml.) by which the solution gradually turbid. After thoroughly saturating hydrogen sulfide, the white precipitate so formed was collected by filtration, the portion of the precipitate soluble in hydrochloric acid was combined with the filtrate, and the solution was evaporated. The residue was neutralized with sodium hydrogen carbonate and yellow crystals (60 mg.), m. p. 289°C (decomp.), were obtained. This was recrystallized from water to yellow needles, m. p. 294°C (decomp.), whose ultraviolet and infrared spectra agreed completely with those of 2-amino-1,3-diazaazulene.

Reaction of III and Potassium Thiocyanate.—To a solution of III (400 mg.) dissolved in water (2.5 ml.) and added with 4 drops of concentrated hydrochloric acid, aqueous solution of potassium thiocyanate (260 mg.) was added and the mixture was heated on a water bath for 15 min. The crystals formed on coolling this solution were collected (460 mg.) and recrystallized from diluted ethanol to brown prisms, XXI, m. p. 179~179.5°C (decomp.).

Found: C, 49.43; H, 3.92; N, 31.45. Calcd. for $C_9H_9N_5S$: C, 49.31; H, 4.14; N, 31.95%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 265(4.50), 300(3.75), 367 (4.34).

Stephens-McFadyen Decomposition of III.—III (50 mg.) was dissolved in 50% acetic acid (4 ml.), to which 10% copper sulfate solution (1.2 ml.) was added. The mixture was then warmed on a water bath, the solution turned yellowish green and nitrogen gas evolved. After 10 min., the reaction mixture was filtered, and the filtrate was neutralized with a solid sodium hydrogen carbonate, extracted with chloroform. The chloroform extracts were evaporated, and the residue was dissolved in benzene and purified through a short column of alumina. The elute gave yellow needles, m. p. 115~118°C, and no depression with authentic 1,3-diazaazulene on mixed fusion.

The author expresses his deep gratitude to Professor Tetsuo Nozoe of the Faculty of Science of this University for kind and unfailing guidance throughout the course of this work. The elementary analyses were performed by Mr. Shinichi Oyama and Miss Ayako Iwanaga. The author wishs to express his thanks to these helps and donations.

The Chemical Research Institute of Non-Aqueous Solutions
Tohoku University
Katahira-cho, Sendai

Non-stoichiometry of Nickel Oxide

By Yoshio IIDA, Kenzo SHIMADA and Shunro OZAKI

(Received March 9, 1960)

The physical and chemical properties of nickel oxide have been studied extensively by many investigators[1]. Gray[2] and Iida[3] reported that the electrical properties of nickel oxide varied with the preparation method. Since nickel oxide is a *p*-type semiconductor containing an excess of oxygen, the change in the electrical properties are thought to be attributed to a concentration of an excess of oxygen which produces cation vacancy in nickel oxide. From the electrical neutrality of the crystal, $2x$ Ni^{3+} ions must be formed when there are x vacancies of Ni^{2+} in the crystal.

In the present experiment, the concentrations of Ni^{3+} ion in nickel oxide crystals prepared from various methods have been determined by chemical analysis and a concentration of cation vacancy has been calculated. The concentration of cation vacancy thus obtained has been compared with that obtained by the density and lattice parameter of nickel oxide.

Experimental

Recrystallized nickel nitrate was prepared by dissolving electro-deposited nickel of 99.9% purity in c. p. nitric acid. Nickel carbonate and nickel hydroxide were precipitated in an aqueous solution of nickel nitrate by ammonium carbonate and ammonium hydroxide. These nickel salts were heated for 3 hr. in air in the temperature range of 400 to 1300°C to obtain nickel oxide.

Electrical resistance was measured in the air from room temperature to 300°C by a method similar to that described by Griffith[4].

The density measurement was the same as that described by Culbertson[5] except that a weighing glass bulb sealed under evacuation was broken off in distilled water containing 0.001% of surface active reagent.

Powder diffraction patterns were recorded by a diffractometer with copper-target radiation. The lattice parameter of nickel oxide was determined by the diffraction peak of (420).

The chemical analysis of Ni^{3+} was made according to the directions of Verwey[6].

The composition ratio of Ni/O was determined by hydrogen reduction of samples at 700°C for 5 hr.

Results and Discussion

Non-stoichiometry of Nickel Oxide Prepared from Nickel Nitrate.—Nickel oxide was prepared by heating nickel nitrate for 3 hr. at temperatures of 400 to 1200°C. Experimental results are shown in Table I. It is seen from electron photographs that particle size increases with an increase in the heating temperature (Fig. 1). At low temperatures of 400 and 500°C, unit particle size can not be determined by an electron photograph because nickel oxide is in the form of very small particles or their aggregates. At 600°C it is about 0.2 μ and grows to 1 μ at 1000°C. Inasmuch as the width of diffraction peak (200) at half intensity did not vary with the heating temperature in the range of 400 to 1200°C, the crystallization of nickel oxide heated at 400 and 500°C is thought to be completed.

The composition ratio of O/Ni is larger than 1 below 600°C and is nearly 1 above 600°C. It is seen that nickel oxide prepared by heating the nitrate below 600°C has obviously an excess of oxygen. The lattice parameter of nickel oxide does not vary with the heating temperature within the experimental error. The density of nickel oxide increases with an increase in the heating temperature as shown in Table I. The change in the lattice parameter is more strongly dependent on the oxygen ion which has a larger ion radius than the nickel ion. From the consideration of a constant lattice parameter and the decreasing densities of nickel oxide with an excess of oxygen, it seems to be reasonable to assume that nickel oxide has a cation vacancy as mentioned previously[7].

It has been known[8] that the Ni^{3+} ion is not present in pure and dry nickel oxide. Chemical analysis, however, shows that the Ni^{3+} ion is evidently present in pure and dry nickel

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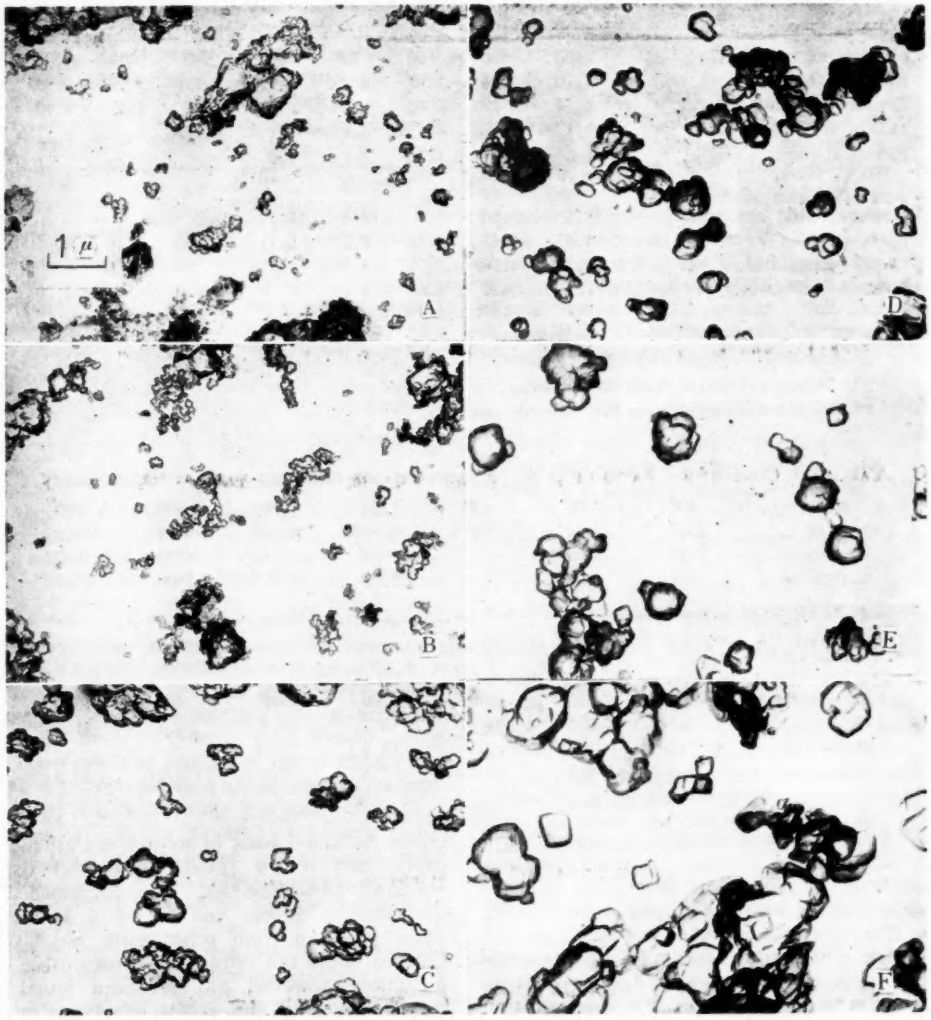

Fig. 1. Electron photographs of nickel oxides prepared by decomposition of nickel nitrate at (A) 400°C, (B) 600°C, (C) 700°C, (D) 800°C, (E) 900°C and (F) 1000°C.

oxide and decreases with the calcining temperature of nickel nitrate. From the reason mentioned above, a concentration of cation vacancy can be calculated as shown in Table I.

From the viewpoint of a semiconducting mechanism, electrical conductivity of nickel oxide should increase with an increase in an excess of oxygen or in a concentration of cation vacancy. The experimental resuls show that the conductivity increases with the cation vacancy. As nickel oxide calcined at low temperatures has a small particle size, the conductivity is thought to increase with an increase in the particle size in view of the contacting resistance of the powder. The conductivity of nickel oxide calcined at low temperatures, however, is high in spite of its small particle size according to the experimental results. Furthermore, Table I shows that the activation energy of the conductivity of nickel oxide decreases with an increase in the cation vacancy. From these facts it is concluded that nickel oxide calcined at low temperatures is obviously a non-stoichiometric compound and has Ni^{3+} ions and cation vacancies, consequently.

Table I shows that the concentration of vacancies calculated from the densities is higher than that from chemical analysis of the

TABLE I. PHYSICAL AND CHEMICAL ANALYSIS OF NICKEL OXIDE PREPARED FROM DECOMPOSITION OF NICKEL NITRATE

Calcining temp., °C	400	500	600	700	800	900	1000	1200
Ratio of O/Ni	1.10	1.04	1.01	0.995	0.995	0.995	0.993	0.995
Density observed, g./cc.	5.74	6.28	6.40	6.48	6.53	6.62	6.65	6.80
Lattice parameter, Å	4.1798	4.1801	4.1792	4.1788	4.1788	4.1788	4.1788	4.1756
Electrical conductivity at 300°C, Ω cm.	6.8×10^{-4}	4.9×10^{-4}	4.1×10^{-4}	2.1×10^{-4}	1.0×10^{-4}			
Activation energy of the conductivity, kcal./mol.	8.5	9.5	10.0	10.3	10.5	11.0	11.4	
Ni^{3+}, at. %	1.07	0.41	0.31	0.27	0.11	0.040	0	0
Density calculated, g./cc.	6.789	6.787	6.792	6.794	6.794	6.794	6.794	6.809
Number* of vacancy per cc.	1.71×10^{21}	1.30×10^{21}	1.00×10^{21}	8.01×10^{20}	6.73×10^{20}	4.42×10^{20}	3.65×10^{20}	2.10×10^{19}
Number** of vacancy per cc.	2.79×10^{20}	1.24×10^{20}	8.62×10^{19}	7.40×10^{19}	3.02×10^{19}	1.09×10^{19}		

* Values calculated from the densities.
** Values calculated from Ni^{3+} atomic per cent.

TABLE II. COMPOSITION RATIO OF O/Ni OF NICKEL OXIDE PREPARED VARIOUS NICKEL SALTS

Calcining temp., °C	400	500	600	700	800	900	1000
Nitrate	1.10	1.04	1.01	0.995	0.995	0.995	0.993
Hydroxide	1.12	1.07		1.02		1.00	0.997
Carbonate	1.21	1.09		1.02		1.00	0.991

TABLE III. ACTIVATION ENERGY OF ELECTRICAL CONDUCTIVITY OF NICKEL OXIDE PREPARED FROM VARIOUS SALTS (kcal./mol.)

Calcining temp., °C	400	500	600	700	800	900	1000
Nitrate	8.5	9.5	10.0	10.3	10.5	11.0	11.4
Hydroxide	7.7	8.3	—	10.3	—	—	—
Carbonate	5.3	6.3	—	7.4	—	8.2	9.3

Ni^{3+} ion. As a measurement is liable to give too low density values to small particles because of the incomplete desorption of gases even under the cautious density measurement, the disagreement may be attributed to the lowering of observed density. Further experiment, however, is necessary to determine which method is better to obtain the concentration of vacancy in nickel oxide.

Effect of Starting Material. —As nitrogen peroxide which may be responsible for an excess of oxygen in nickel oxide may be formed when nickel nitrate is decomposed, it is of interest to know whether the excess of oxygen in nickel oxide can be formed when nickel carbonate or nickel hydroxide is decomposed. Table II shows that the excess of oxygen is formed in the nickel oxides prepared from nickel carbonate and hydroxide as well as from nitrate. It is seen that the excess of oxygen is higher in nickel oxide from carbonate than in nickel oxides from nitrate and hydroxide. Electrical conductivity measurement shows that the activation energy of electrical conductivity decreases with an increase in the excess of oxygen for all nickel oxides and is the lowest for nickel oxide obtained from carbonate. It is confirmed that the excess of oxygen can be formd in nickel oxide prepared from other salts which are different from the nitrate. No reasonable explanation, however, has yet been found to make clear why the excess of oxygen is the highest in nickel oxide from carbonate, although nickel carbonate, hydroxide and nitrate start to decompose at about 250°C and their purity is essentially the same.

Isothermal Change in Electrical Conductivity. —From the above experiments, it has been evident that the nickel oxide obtained by heating nickel salts at low temperatures exhibits a vacant cation structure and its electrical properties vary with the cation vacancy and the concentration of cation vacancy decreases with the increasing heating temperature. It seems to be desirable to determine the isothermal change in electrical conductivity of the nickel oxide. Nickel nitrate was heated at 300°C for 3 hr. to obtain nickel oxide with a high concentration of the vacancy whose ratio of O/Ni

is 1.36. The isothermal change in the electrical conductivity at 300, 400 and 500°C is shown in Fig. 2. It is seen that the behavior of electrical conductivity varies with heating temperature. At 300°C, the electrical conductivity increases with the heating time while it

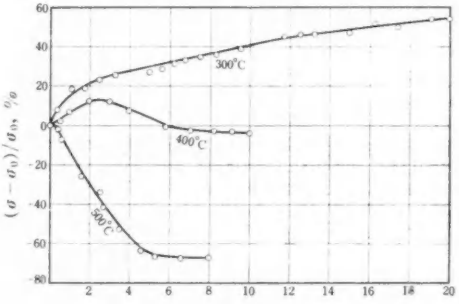

Fig. 2. The isothermal change in electrical conductivity of nickel oxide at various temperatures. Nickel oxide was made by decomposition of nickel nitrate at 300°C for 3 hr.

decreases with the heating time at 500°C. At 400°C, the conductivity increases initially in a heating period of 2 hr. and then decreases with the time. Since the cation deficient structure of nickel oxide is thought to be formed during the decomposition process of nickel nitrate and to be uncompleted in 3 hr. at 300°C, the conductivity increases with the time when it is reheated at 300°C. At 400°C, the uncompleted cation deficient structure is completed in an initial heating period. This may be the result in the initial inrease in the conductivity at 400°C.

The cation deficient structure of nickel oxide is expressed by the following equation according to Hauffe[9]

$$NiO + 2\oplus + \square'' \rightleftharpoons \frac{1}{2}O_2$$

where $\square''$ represents the vacancy of nickel site and $\oplus$, a positive hole of the electron. There are equilibrium states at various temperatures between the concentration of the vacancy and oxygen pressure following the above equation. Since nickel oxide calcined at 300°C has a higher concentration of vacancy than the equilibrium state at 400°C, the vacancies greater than the equilibrium value diffuse to the surface of the crystal and disappear. The decreasing conductivity at 400°C in Fig. 2 can be explained by the diffusion of vacancy.

Summary

Nickel oxide obtained by heating nickel nitrate, carbonate and hydroxide at low temperatures exhibits a non-stoichiometric structure. An excess of oxygen decreases with an increase in the heating temperature of nickel salts. Concentration of Ni^{3+} determined by chemical analysis increases with the excess of oxygen. Densities of nickel oxide or activation energy of electrical conductivity decrease with an increase in the excess of oxygen, whereas lattice parameter does not vary. Isothermal change in electrical conductivity of nickel oxide shows that the decrease in vacancies may be attributed to the diffusion of vacancies to the crystal surface. The concentration of vacancies calculated from the density is higher than that from the concentration of Ni^{3+} ion. The disagreement may be attributed to the density measurement technique.

Government Industrial Research Institute
Kita-ku, Nagoya

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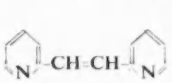
Geometrical Isomers of 1,2-Bis-(4-pyridyl)-ethylene

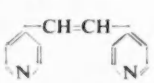
By Takumi KATSUMOTO

(Received March 11, 1960)

In the preceding paper[1] the author reported the geometrical isomers of 1,2-bis-(2-pyridyl)-ethylene. Regarding 1,2-bis-(4-pyridyl)-ethylene, it is also expected that it will be able to exhibit geometrical isomerism and then to prove its existence in a cis and a trans form. Hitherto, however only one species[2,3] which melts at 151~152°C has been known. The author condensed 4-picoline and 4-pyridylaldehyde into 1,2-bis-(4-pyridyl)-ethylene and then separated two isomers from the ethylene, one corresponding to the known species and the other to the unknown one. The elementary analyses, molecular weight, melting points and ultraviolet and infrared absorptions, all prove that the former is a trans isomer and the latter a cis isomer of 1,2-bis-(4-pyridyl)ethylene.



1,2-Bis-(2-pyridyl)-ethylene



1,2-Bis-(4-pyridyl)-ethylene

Experimental

Synthesis of 1,2-Bis-(4-pyridyl)-ethylene.—The ethylene was synthesized from 4-pyridylaldehyde, 4-picoline and anhydrous zinc chloride according to Thayer and Corson's method[2]. 4-Pyridylaldehyde from the Aldrich Chemicals was distilled under 16 mmHg pressure and the fraction boiling at 85.5°C was used; the phenylhydrazone, m. p. 177.0~178.5°C (lit., 178~179°C[4]). 4-Picoline was separated from the "β-picoline", b. p. 140~148°C, according to the following method[5]. The "β-picoline" contains 3-picoline, 4-picoline and 2,6-lutidine. 2,6-Lutidine was first removed as the urea adduct[6], and then the mixture of the unchanged 3- and 4-picoline was converted into their oxalates[7]. 4-Picoline oxalate was separated by the fractional crystallization from the absolute alcohol solution, as it is less soluble in absolute ethanol than 3-picoline oxalate; 4-picoline oxalate, m. p. 138~139°C. 4-Picoline was recovered by the decomposition of the oxalate with sodium hydroxide and distilled; b. p. 145.0~146.0°C; picrate, m. p. 165.5~166.5C. The infrared absorption spectra of the 4-pyridylaldehyde and the 4-picoline showed the complete absence of the 2- and the 3-isomer, respectively in them. 4-Pyridylaldehyde (0.022 mol.), was heated with the equivaleat moles of 4-picoline and anhydrous zinc chloride in a sealed tube at 200~215°C for 16 hr. The reaction mixture was cooled, dissolved in 40 cc. of 3 N sulfuric acid, and basified with sodium hydroxide. The cooled alkaline solution was extracted twice with 30 cc. portion of ether and four times with 30 cc. portions of chloroform. The chloroform extract was dried over anhydrous potassium carbonate. After the greater part of the solvent was removed, the concentrated chloroform extract was chromatographed on a column (2×40 cm.) of alumina and the column was eluted with chloroform. The chromatograph afforded a satisfactory fractionation. One (**A**), eluted first, formed colorless, long needles, which melted at 151.5~152.5°C after three additional recrystallizations from water and corresponds to the known species of the ethylene. Yield, 17% theoretical. The other (**B**), contained in the next eluate, formed colorless, viscid oil and crystallized by being scratched with a sharp glass rod. The repeated recrystallizations of the crystals from cyclohexane-benzene (1:1) gave colorless, small needles, m. p. 110~111°C. Yield, 17.5% theoretical.

Measurements.—Molecular weight was determined by Rast's method. The ultraviolet absorption spectra (in absolute ethanol) were made with a Shimadzu QB-50 quartz spectrophotometer. The wavelengths of the photometer were calibrated with the absorption band at 301 mμ of an aqueous potassium nitrate solution. The infrared absorption spectra were obtained with a Shimadzu IR spectrophotometer equipped with a rock-salt prism. Readings were taken in the range 2000~670 cm^{-1} and calibrated with the absorption bands of polystyrene.

Results and Discussion

As described above, **A** is colorless, long needles and melts at 151.5~152.5°C, while **B** is colorless, small needles and melts at 110.0~111.0°C. **A** is identified with the known species of 1,2-bis-(4-pyridyl)-ethylene, as the melting point is in good agreement with the published value of the ethylene (lit., 151~152°C[2]) and the result of the elementary analyses is consistent with the calculated value for the ethylene $C_{12}H_{10}N_2$ (Table I). Furthermore, the assignment of the infrared

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TABLE I. COMPARISON OF THE TWO ISOMERS OF 1,2-BIS-(4-PYRIDYL)-ETHYLENE

Compound	A long needles	B small needles
M.p.	151.5~152.5°C	110.0~111.0°C
Elementary analyses		
Found	C: 78.9 % H: 5.75 N: 15.60	C: 79.0 % H: 5.83 N: 15.20
Calcd. for $C_{12}H_{10}N_2$	C: 79.1 % H: 5.53 N: 15.40	
Molecular weight		
Found	—	188
Calcd. for $C_{12}H_{10}N_2$		182

spectrum makes sure of the above determination, as is described later. The elementary analyses and molecular weight of B are also consistent with the calculated values for the ethylene (Table II); thus **B** is an isomer of **A**. Thayer et al. reported that 1,2-bis-(4-pyridyl)-ethane melted at 110~111°C, which is the same temperature at which **B** melts. Although there is little possibility of producing the ethane in our experimentation, the author has proved that **B** is quite different from the ethane by the mixed examination and the infrared absorption spectra in carbon disulfide as follows; the ethane from the Aldrich Chemicals (m. p. 111~112°C) depresses largely the melting point of **B** in the mixed examination and it shows no absorption in the range 830~670 cm^{-1}, while **B** absorbs strongly at 763 cm^{-1}.

The infrared absorption spectra of the two isomers, **A** and **B**, are shown in Table II and Fig. 1. They resemble each other very closely except for a few absorptions. **A** and **B** give the following common absorptions; four absorptions in the range 1630~1430 cm^{-1} due to the double bond stretching vibrations of the pyridine ring, three absorptions in the range 1250~950 cm^{-1} due to the C-H in-plane bending vibrations of the 4-substituted pyridine ring and one strong absorption in the range 790~830 cm^{-1} due to the C-H out-of-plane bending vibration of the 4-substituted pyridine ring, respectively[8,9,10]. These absorptions lie always in the range indicated by Shindo[8] and Katritzky[9] for the above vibration modes of the 4-substituted pyridine, as shown in the last column of Table II. A few absorptions that are not common to them arise from the disubstituted ethylene as will be discussed later. No other significant absorptions are found in the spectra. Thus, it is certain that **A** and **B** are the disubstituted ethylenes with 4-pyridyl radicals, i.e. 1,2-bis-(4-pyridyl)-ethylenes and the geometrical isomers with each other.

The geometrical arrangements of **A** and **B** are determined by the infrared and ultraviolet absorption spectra, the melting points, and the solubilities in organic solvents.

TABLE II. INFRARED ABSORPTION BANDS OF 1,2-BIS-(4-PYRIDYL)-ETHYLENE

A (trans) cm^{-1}	A (trans) ε	B (cis) cm^{-1}	B (cis) ε	Assignment*	Reference range
1595	234	1603	206	PR-1	
1560	51	1567	57	PR-2	four bands in the range
1504	24	1508	17	PR-3	1630~1430 cm^{-1}
		1458	24		
1418	106	1420	111	PR-4	
1289	29			EHI (*trans*)	1310~1290[13]
1242	51	1242	38	PHI-1	1232~1211[8]
1070	24	1070	34	PHI-2	1070~1053[8]
					1072~1055[9]
995	94	997	66	PHI-3	1003~ 990[8]
					997~ 985[9]
966	145			EHO (*trans*)	990~ 965[12]
951	61				
837	104				
821	182	819	103	PHO	790~ 830[11]
		805	66		
		763	190	EHO (*cis*)	800~ 650[11]

* PR means the stretching vibration of a pyridine ring; EHI and PHI mean the in-plane bending vibrations and EHO and PHO mean the out-of-plane bending vibrations of the hydrogen atoms remaining on an ethylene and a pyridine ring, respectively.

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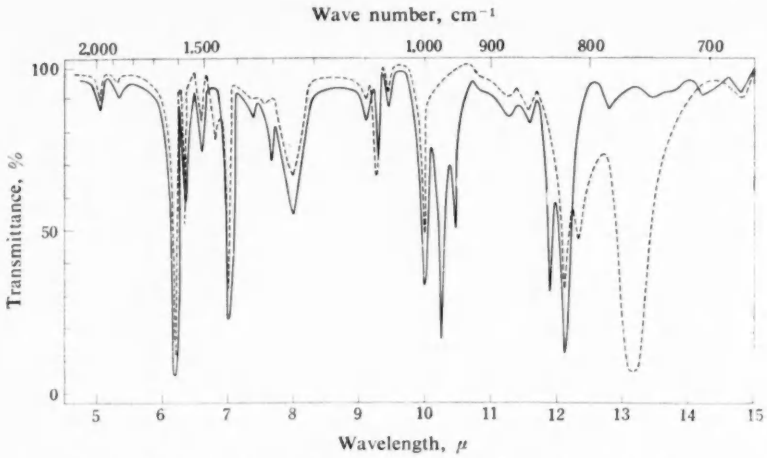


Fig. 1. Infrared absorption spectra of 1,2-bis-(4-pyridyl)-ethylene.
A 5 μ~12.5 μ (chloroform), 12.5~15 μ (acetone).
B 5 μ~12.5 μ (chloroform), 12.5~15 μ (carbon disulfide).
—— A (trans), ------ B (cis)

TABLE III. ULTRAVIOLET ABSORPTION BANDS OF 1,2-BIS-(4-PYRIDYL)-ETHYLENE (in absolute ethanol)

	E-band		K-band	
	λ_{max}	ε_{max}	λ_{max}	ε_{max}
cis Form (**B**)	212 mμ	8,390	257 mμ	4,210
trans Form (**A**)	218 mμ	11,460	288 mμ	32,490
	223	11,990	299	33,380
			312	19,470

The infrared absorptions due to the cis- and the trans form are quite different[11]. trans isomers absorb strongly close to 965 cm^{-1} and weakly in the range 1310~1290 cm^{-1}. Rasmussen and Brattain showed that the former absorptions appear only with the trans double bond[12]. This absorption is attributed to the =C-H out-of-plane bending vibration, and the latter to the in-plane bending vibration, of the *trans*-disubstituted ethylene[13]. Cis isomers give no absorptions in this range. **A** gives the two absorptions at 966 cm^{-1} and 1298 cm^{-1}, but the absorptions corresponding to them cannot be found in the spectrum of **B**. While, Zechmeister[14] suggested the *cis*-disubstituted ethylenes conjugated with double bonds on both sides give an absorption near 780 cm^{-1}. **B** absorbs strongly at 763 cm^{-1} as described above and **A** gives no absorptions in the regions. These absorptions suggest that **A** is a trans isomer and **B** is a cis isomer.

The melting point of **B** is lower by about forty degrees than that of **A**, as shown in

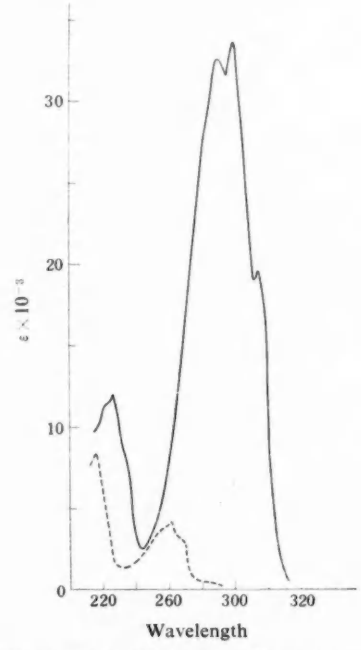


Fig. 2. Ultraviolet absorption spectra of 1,2-bis-(4-pyridyl)-ethylene.
—— A (trans), ---- B (cis)

11) L. J. Bellamy, "The Infrared Spectra of Complex Molecule", 2nd Ed., Methuen, London (1958), p. 45.
12) R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 131, 135 (1947).
13) N. Sheppard and G. Sutherland, *Proc. Roy. Soc.* **A196**, 195 (1949).
14) L. Zechmeister et al., *Acta Chem. Scand.*, **8**, 1421 (1954).

Table I. As the cis isomer always melts at a very much lower temperature than trans isomer does, **B** and **A** seem to be a cis and a trans isomer, respectively. The polar substance like a cis isomer is not easily dissolved in the non-polar solvents. **B** is insoluble in cyclohexane, while **A** is readily soluble in it. **B** seems to be a cis isomer.

Regarding the conjugation band of the ultraviolet absorption spectra, a cis isomer gives the spectrum similar to the sum of the spectrum of the component parts of the molecule on the either side of the double bond. The bathochromic displacement and much increase of the absorption intensity of the conjugation band always occur on passing from the cis structure to the trans structure. The ultraviolet absorption spectra of **A** and **B** are shown in Table III and Fig. 2. The conjugation band of 4-picoline has the intensity of some 2.000 at 255 mμ and that of **B** has about two times as much intensity of 4,210 as the former at 257 mμ. While **A** gives the band at 299 mμ with intensity 33,380. The ultraviolet absorption spectra of **A** and **B** are typical of the trans and the cis structure.

The conclusion is that the known species of 1, 2-bis-(4-pyridyl)-ethylene (**A**) is the trans isomer and another species (**B**) which was separated by the present author is the cis isomer.

The author wishes to thank Professor S. Kimura of Kyoto University for encouragement, Professor T. Matsu'ura of Hiroshima University for recording infrared spectra and Mr. Yamaguchi of this laboratory for his helpful assistance.

Chemical Laboratory
Kwansei Gakuin University
Nishinomiya, Hyogo

γ-Hydroxyarginine, a New Guanidino Compound from a Sea-cucumber. II. Determination of the Configuration

By Yoshimasa FUJITA

(Received March 21, 1960)

A new guanidino compound was first discovered in a sea-cucumber, *polycheira rufescence*[1], and then isolated purely and identified as γ-hydroxy-L-arginine (**I**)[2]. The compound contains two asymmetric carbon atoms (α and γ) and should, therefore, exist theoretically in four stereoisomeric forms. In the preceding paper[2] it was concluded that the configuration on the α-carbon is the L-form[3] in view of the susceptibility to arginase[4] and L-amino acid oxidase[5], whereas that on the γ-carbon was not yet decided. The conclusion was further supported by Makisumi[6] in our laboratory. He observed that **I** was quantitatively decarboxylated by the action of L-arginine decarboxylase from *E. coli* 7020[7].

In contrast with γ-hydroxyarginine, γ-hydroxyornithine was studied in detail with regard to its stereoisomers by Witkop et al.[8,9]. They proved that *erythro-* and *threo*-γ-hydroxy-L-ornithine were stereochemically equivalent to hydroxy-L-proline and allohydroxy-L-proline, respectively.

In the present study, the configuration on the γ-carbon was established according to the method of Witkop et al.[8] with a slight modification. γ-Hydroxy-L-ornithine (**II**) produced from **I** by the action of arginase was treated first with nitrosyl chloride, and then with barium hydroxide. From this reaction mixture, a product which gave a yellow spot with ninhydrin reagent on a paper chromatogram was isolated by fractionation on a column of Amberlite CG-120. The product was identified

1) H. Sasaki, Y. Fujita, S. Makisumi and S. Shibuya, *J. Japanese Biochem. Soc.* (*Seikagaku*), **30**, 642 (1958).
2) Y. Fujita, This Bulletin, **32**, 439 (1959).
3) E. J. Crane, *Chem. Eng. News*, **25**, 1363 (1947).
4) D. M. Greenberg, "The Enzymes", Vol. I, edited by J. B. Sumner and K. Myrbäck, Academic Press Inc., New York (1951), p. 894.
5) Y. Robin, *Bull. Soc. Chim. Biol.*, **35**, 285 (1953). H. Blashko and D. B. Hope, *Biochem. J.*, **62**, 335 (1956).
6) S. Makisumi, unpublished data.
7) E. F. Gale, *Biochem. J.*, **41**, vii (1947). S. M. Birnbaum and J. P. Greenstein, *Arch. Biochem. Biophys.*, **39**, 108 (1952).
8) B. Witkop and T. Beiler, *J. Am. Chem. Soc.*, **78**, 2882 (1956).
9) B. Witkop, *Special Publication No. 3.*, The Chemical Society, Burlington House, W. 1, London, (1955), p. 60.

as allohydroxy-D-proline (III). The optical purity of III was assured with the aid of column chromatography (Fig. 2).

The fact that a compound having the L$_S$ configuration as to the α-carbon atom converts by the action of a certain reagent into a product having the D$_S$ configuration, suggests that it is a result of the Walden inversion. According to the extensive studies by Izumiya et al.[10] on the Walden inversion of α-amino acid, it is generally accepted that in an α-amino acid possessing a secondary carbon atom at β-position the inversion does not occur by the halogenation with nitrosyl halide, but takes place on treating the resulting α-halogeno acid with basic reagents such as ammonia.

When, as in the case of the present experiment, nitrosyl chloride acts on II, there is a possibility that three chlorinated acids (α-chloro-δ-amino-γ-hydroxyvaleric, δ-chloro-α-amino-γ-hydroxyvaleric, and α,δ-dichloro-γ-hydroxyvaleric acids) are produced therefrom. Of the three acids, α-chloroacid and δ-chloroacid are concerned in the formation of hydroxyproline after cyclization. The composition of the reaction mixture was, therefore, examined by means of determination of the total nitrogen, carbon dioxide liberated with Chloramine T and chloride ions (Table I). The results indicated that the amount of α-chloroacid was much grater than that of δ-chloroacid, showing a preferential reactivity of the α-amino group of II. It is reasonable, as in the cases of chain compound, that the inversion should also occur in the stage of a base-catalyzed cyclization of α-chloro-δ-amino-γ-hydroxyvaleric acid. Accordingly, the allohydroxy-D-proline obtained by the inversion can be established as originating from *erythro*-γ-hydroxy-L-ornithine. The latter compound, if the inversion did not occur, would convert into hydroxy-L-proline (IV). Therefore, the whole configuration of I should, as a matter of course, be concluded to be *erythro*-γ-hydroxy-L-arginine.

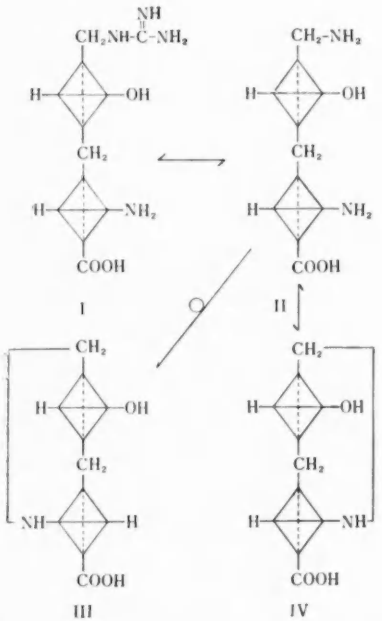


Fig. 1. Stereochemical correlation between γ-hydroxyarginine, γ-hydroxyornithine and (allo)hydroxyproline.
⟷ Stereochemical equivalence
∠Ω Walden inversion

Experimental

Material. — The γ-hydroxy-L-ornithine hydrochloride used in the present study was prepared from γ-hydroxy-L-arginine hydrochloride by the action of arginase[2]: m. p. 182~183°C (decomp.), $[\alpha]_D^{19}$ +10.6° (*c* 5, in water)[11].

According to Witkop et al.[5], in the conversion of γ-hydroxyornithine to (allo)hydroxyproline different results are obtained by using either the open acid or the lactone as the starting material. Therefore, whether or not contaminated with lactonized γ-hydroxyornithine, the material was checked by determining the carbon dioxide evolved with Chloramine T at pH 4.7 and 25°C. On mixing γ-hydroxyornithine with the reagent, a brisk evolution of the gas was observed. This amounted to 90% after 5 min. and to 100% after 15 min. The observation was in good accordance with that of Witkop on the open acid.

Conversion of γ-Hydroxy-L-ornithine to Allohydroxy-D-proline. — A nitrosyl chloride solution (6 ml.) prepared according to Witkop et al.[5] was added drop by drop to an ice-cold solution of γ-hydroxy-L-ornithine hydrochloride (185 mg.) dissolved in 9 N hydrochloric acid (10 ml.). The reaction mixture was stirred for 10 min. in the cold and then heated at 55°C for 20 min., followed by evaporation to dryness in vacuo. The residue was dissolved in water (2 ml.), and heated with 0.2 N barium hydroxide solution (10 ml.) in a boiling water bath for 10 min. The solution was freed from barium by neutralizing with sulfuric acid and centrifugation. The supernatant solution was passed through a column of Amberlite CG-120 (H-form, 1×18 cm.). The adsorbed substances were eluted with 0.2 N hydrochloric acid (15 ml./hr.), and collected in 5 ml. fractions. Each fraction was analyzed by paper chromatography and only the fractions (31st to 40th tubes) which gave a single yellow spot with ninhydrin were united. The resulting solution was evaporated up to dryness in

10) N. Izumiya et al., *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **72**, 26, 149, 445, 550, 1050 (1951); This Bulletin, **25**, 265 (1952); **26**, 53 (1953).

11) The author wishes to correct the erroneous figure for the specific rotation described in Ref. 2.

vacuo. The crystalline residue was dissolved in a small volume of water and the solution was passed through a column of Amberlite IR-4B (OH-form). The effluent freed from chloride by this treatment was again concentrated in vacuo and the crystalline residue was triturated with methanol (2 ml.), filtration and washing with methanol and ether being followed. The product was recrystallized from water-ethanol. Yield 31 mg.; m. p. 237~239°C (decomp.); $[\alpha]_D^{15}$ +57.0° (*c* 1, in water).

Found: C, 45.87; H, 6.78; N, 10.86. Calcd. for $C_5H_9NO_3$: C, 45.80; H, 6.92; N, 10.68%.

The above product (1 mg.) dissolved in citrate buffer pH 3.20 (1 ml.) was passed through a column of Dowex 50-X8 (0.9×50 cm.)[12,13] maintained at 37°C, and eluted (4 ml./hr.) with the same buffer. The effluent was collected in 1 ml. fractions and each fraction was analyzed by ninhydrin colorimetry[14]. The elution pattern of the product had a single peak which corresponded to allohydroxyproline and no other peak was observed, while the authentic mixture of hydroxyproline and allohydroxyproline[15] was completely resolved into two peaks under the same condition (Fig. 2).

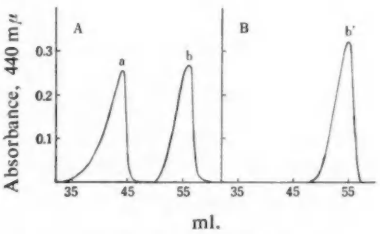


Fig. 2. The elution pattern of hydroxyproline (HP) and allohydroxyproline (AHP) from a column of Dowex-50 (0.9×50 cm.) at pH 3.20 and 37°C.
A: Authentic mixture of L-HP (a) and D-AHP (b)
B: D-AHP (b') prepared by cyclization from γ-hydroxy-L-ornithine

12) S. Moore and W. H. Stein, *J. Biol. Chem.*, **192**, 663 (1951).
13) K. A. Piez, *J. Biol. Chem.*, **207**, 77 (1954).
14) E. W. Yemm and E. C. Cocking, *Analyst*, **80**, 209 (1955); *Biochem. J.*, **58**, xii (1954).
15) The author is indebted to Dr. S. M. Birnbaum and Dr. M. Winitz for a generous supply of the sample of hydroxy-L-proline and allohydroxy-D-proline, respectively.

Composition of the Reaction Mixture with Nitrosyl Chloride. — A solution of γ-hydroxy-L-ornithine hydrochloride (100 mg.) was treated with a nitrosyl chloride solution (3 ml.) as described above. The reaction mixture was evaporated up to dryness in vacuo and further dried in a vacuum desiccator on potassium hydroxide until it reached a constant weight. It was analyzed for total nitrogen by the micro Kieldahl method, for the liberation of carbon dioxide with Chloramine T at 25°C in a Warburg manometer and for chloride by the titration with silver nitrate[16]. The following values were obtained: 5.32% total nitrogen, 4.12% CO_2 and 13.43% Cl^-. The results were summarized in Table I.

Table I. Composition of the reaction mixture with nitrosyl chloride

Symbol*	Mol. wt.	Theory, % N_2	CO_2	Cl^-	Composition of the reaction mixture, %
W	221.09	12.7	19.9	32.1	20
X	204.06	6.9	0	17.4	39
Y	204.06	6.9	21.6	17.4	1
Z	187.03	0	0	0	40

* W: γ-Hydroxyornithine·2HCl
X: α-Chloro-δ-amino acid·HCl
Y: δ-Chloro-α-amino acid·HCl
Z: α,δ-Dichloro acid

The figures for W, X, Y and Z in Table I were calculated from the following equations: 12.7W+6.9X+6.9Y=5.32; 19.9W+21.6Y=4.12; 32.1W+17.4X+17.4Y=13.43; W+X+Y+Z=1.

The author wishes to express his cordial thanks to Professor S. Shibuya for his guidance and encouragement, and to Assistant Professor N. Izumiya for his advice. His thanks are also due to the Ministry of Education for financial support of this research.

Laboratory of Biochemistry
Faculty of Science
Kyushu University
Fukuoka

16) S. Ueo and S. Sakamoto, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **58**, 711 (1938).

The Dehydration Reactions of Nitroparaffins and Aldoximes

By Teruaki MUKAIYAMA and Tsujiaki HATA

(Received May 4, 1960)

The preceding paper[1] describes the reaction of primary nitroparaffin with isocyanate which gives *sym*-disubstituted urea, furoxane and carbon dioxide in excellent yields in the presence of a catalytic amount of tertiary amine.

$$4R\text{-}N{=}C{=}O + 2R'CH_2NO_2 \xrightarrow{R_3N} 2RHNCONHR + 2CO_2 + R'C(=N(\to O)O)C(=O)R' \quad (1)$$

This reaction proceeds to the formation of disubstituted urea and furoxane through intermediates or amine and nitrile oxide which are formed by the decomposition of the addition compound of isocyanate and *aci*-nitroparaffin with spontaneous evolution of carbon dioxide. The reaction of the amine with isocyanate yields di-substituted urea and furoxane is formed by the dimerization of nitrile oxide.

Nitrile oxide, one of the two intermediates, was confirmed by the formation of isoxazoline when isocyanate, nitroparaffin and tertiary amine are reacted in the presence of unsaturated compound as shown in the following equation.

$$RCH_2NO_2 + CH_2{=}CH\text{-}OAc + 2R'\text{-}N{=}C{=}O \xrightarrow{R_3N} CO_2 + R'HNCONHR' + CH_2(-CH(-OAc)-)C(=O)N(-R) \quad (2)$$

These two reactions 1 and 2 involve initial formation of nitrile oxide by the dehydration of nitroparaffiin with isocyanate and this suggests an interesting study of the dehydration of nitroparaffin with the other organic reagents. Three organic reagents were used to check the dehydration process of nitroparaffins. Firstly, the reaction of primary nitroparaffin with carbodiimide[2] is studied because of its similar behavior to isocyanate. When di-*p*-tolyl carbodiimide and phenylnitromethane are reacted in the presence of tertiary alkyl amine, *sym*-di-*p*-tolylurea and 3-phenyl-4-*p*-tolyl-5-*p*-tolylimino-oxadiazole are obtained (Eq. 3).

$$2CH_3C_6H_4N{=}C{=}N\text{-}C_6H_4CH_3 + C_6H_5CH_2NO_2 \xrightarrow{R_3N} CH_3C_6H_4NHCONHC_6H_4CH_3 + CH_3C_6H_4N(-C(=O)N(-C_6H_5))-N{=}C{=}N\text{-}C_6H_4CH_3 \quad (3)$$

The reaction is satisfactorily explained by the same consideration described in the case of isocyanate which involves the initial formation of nitronate ion by the interaction of nitroparaffin with tertiary amine. One of the oxygen atoms of the nitro group combines in turn with the positively charged carbon of carbodiimide, forming the addition compound I shown in the next scheme.

$$R''_3N + RCH_2NO_2 \rightleftharpoons R''_3\overset{+}{N}H + \left[R\text{-}C(H)=N(\to O)\text{-}O^- \longleftrightarrow R\text{-}C(H)(-O^-)\text{-}N{=}O\right] \xrightarrow{R'N=C=N-R'} R\text{-}C(H)(-O)\text{-}N{=}C(H)\text{-}N(H)\text{-}R' \quad (1)$$

By transferring the hydrogen atom attached to the carbon as a proton, the adduct I decomposes to nitrile oxide and isourea. The latter readily isomerizes to urea and the nitrile oxide adds to carbodiimide, forming oxadiazolone-anil.

$$(1) \begin{cases} \xrightarrow{} CH_3C_6H_4\text{-}N(H)\text{-}C(OH){=}N\text{-}C_6H_4\text{-}CH_3 \xrightarrow{} CH_3\text{-}C_6H_4N(H)\text{-}C(=O)\text{-}N(H)\text{-}C_6H_4CH_3 \\ C_6H_5C{\equiv}N{\to}O \xrightarrow{CH_3C_6H_4N=C=NC_6H_4CH_3} CH_3C_6H_4\text{-}N(-C(=O)N(-C_6H_5))\text{-}C{=}N\text{-}C_6H_4CH_3 \end{cases}$$

1) T. Mukaiyama and T. Hoshino, *J. Am. Chem. Soc.*, in press.

2) H. G. Khorana, *Chem. Revs.*, 53, 145 (1953).

From the above result it appears interesting to extend the dehydration reaction to aldoxime which has a structure similar to that of *aci*-nitroparaffin. When aldoximes and carbodiimide react with each other, *sym*-disubstituted urea and corresponding nitriles result in high yields either in the absence or the presence of tertiary amine according to the Eq. 4.

$$\begin{aligned} &R\text{-}CH{=}NOH + R'\text{-}N{=}C{=}N\text{-}R' \\ &\longrightarrow R'HNC(ON{=}HC\text{-}R){=}NR' \quad (II) \\ &\longrightarrow R\text{-}C{\equiv}N + R'HNCONHR' \end{aligned} \tag{4}$$

Unlike the case of nitroparaffin, the dehydration of aldoxime is carried out even in the absence of catalyst. This would be rationalized if the intermediate II is considered to be formed by the addition of aldoxime, which contains a reactive hydroxyl group in itself, to carbodiimide.

Secondly, the reactions of nitroparaffin and aldoxime with acetylenic ether which is known as a strong dehydrating agent were tested, and the similar results were obtained[3,4]. When *n*-butyl acetylenic ether and phenylnitromethane are reacted in the presence of tertiary alkyl amine, *n*-butyl acetate and 3-phenyl-5-*n*-butoxy-isoxazole are obtained along with by-product, i. e. 3, 4, 5-triphenylisoxazole, formed by the self-condensation of phenylnitromethane[5].

$$\begin{aligned} &HC{\equiv}C\text{-}O\text{-}n\text{-}Bu + C_6H_5CH_2NO_2 \\ &\longrightarrow CH_3COO\text{-}n\text{-}Bu + HC{=}C(C_6H_5{-}C(O){=}N)\text{-}O\text{-}n\text{-}Bu \\ &- C_6H_5C{=}C(C(O){=}N{-}C_6H_5)\text{-}C_6H_5 \end{aligned} \tag{5}$$

The reaction can be understood by considering the addition compound III formed by the addition of the nitronate ion of nitroparaffin to acetylenic ether. By transferring a hydrogen atom, this decomposes to nitrile oxide and enolic derivative of ester. The latter readily isomerizes to ester, and the nitrile oxide adds to acetylenic ether to form isoxazole.

$$C_6H_5CH_2NO_2 \xrightarrow[R_3N]{} [C_6H_5CH{=}NO_2]^-R_3N^+H \xrightarrow{HC{\equiv}C\text{-}OnBu} \underset{C_6H_5\text{-}C(H){=}N(O){\rightarrow}O}{H_2C{=}C(O\text{-}nBu)} \quad (III)$$

$$\longrightarrow H_2C{=}C(OH)\text{-}OnBu \longrightarrow H_2C\text{-}C(=O)\text{-}OnBu$$

$$C_6H_5C{\equiv}N{\rightarrow}O \xrightarrow{HC{\equiv}C\text{-}OnBu} HC{=}C(C(O){=}N{-}C_6H_5)\text{-}OnBu$$

Aldoxime reacts with acetylenic ether to give ester and nitrile in high yields at room temperature in the absence of tertiary amine probably through intermediate IV.

$$\begin{aligned} &HC{\equiv}C\text{-}OR + R'CH{=}NOH \\ &\longrightarrow H_2C{=}C(ON{=}CHR')\text{-}OR \longrightarrow CH_3COOR + R'C{\equiv}N \quad (IV) \end{aligned} \tag{6}$$

Thirdly, further study on the dehydration of aldoxime with ketene acetal[6] which reacts with water to form ester and alcohol was tested. In the presence of a catalytic amount of boron trifluoride and yellow mercuric oxide, the reaction of benzaldoxime and methyl ketene diethyl acetal gives two dehydrated products, benzonitrile and benzoisonitrile, in nearly the same amount, along with ethyl propionate and ethyl orthopropionate. The unexpected formation of benzoisonitrile is of much interesting and this rearrangement found in this reaction is considered to be the simplest model of the Beckmann rearrangement.

$$C_6H_5CH{=}NOH \quad C_6H_5\text{-}C(H){=}N(O) \longrightarrow \begin{cases} C_6H_5C{\equiv}N + C_6H_5N{=}C: \\ CH_3CH_2C(=O)\text{-}OEt + EtOH \end{cases}$$

$$CH_3CH{=}C(OEt)(OEt) \quad CH_3CH_2\text{-}C(OEt)(OEt) \quad (V) \quad CH_3CH{=}C(OEt)(OEt) \longrightarrow CH_3CH_2\text{-}C(OEt)_3$$

Although the addition compound V can not be isolated when benzaldoxime and the ketene acetal are reacted in the presence of the said catalysts, it can be produced in good yield by reacting them either in the presence of triethylamine or in the absence of a catalyst. When the addition compound thus obtained is decomposed in the presence of boron trifluoride and mercuric oxide, both benzoisonitrile and benzonitrile are obtained. But when the adduct is decomposed in the presence of boron trifluoride alone, benzoisonitrile is not obtained

3) J. F. Arens and T. Doornbos, *Rec. trav. chim.* **74**, 79 (1955).
4) T. L. Jacobs, R. Cramer and J. E. Hanson, *J. Am. Chem. Soc.*, **64**, 223 (1942).
5) W. R. Dunstan and T. S. Dymond, *J. Chem. Soc.*, **59**, 410 (1891); S. B. Lippincott, *J. Am. Chem. Soc.*, **62**, 2604 (1940).
6) S. M. McElvain, *Chem. Revs.*, **45**, 453 (1949).

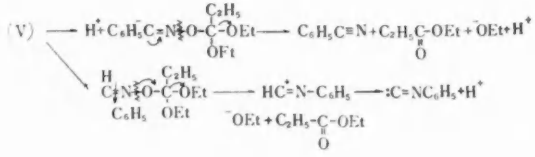
and benzonitrile is exclusively obtained. And no reaction is observed when only mercuric oxide is used. This gives the conclusion that the coexistence of boron trifluoride and mercuric oxide is a necessary condition for the formation of isonitrile.

$$V \xrightarrow{BF_3} C_6H_5C{\equiv}N + CH_3CH_2COOC_2H_5$$

$$V \xrightarrow{HgO} \text{no reaction}$$

Since it has been confirmed that the reaction of aliphatic aldoxime or *n*-heptanaldoxime and ketene acetal gives only nitrile under the same condition, the above-mentioned rearrangement is surely one of the characteristics of aromatic aldoximes.

The course of the rearrangement can be shown by the following scheme.



The addition compound V containing three oxygen atoms attached to one carbon atom has two pathways of decomposition, namely the decomposition with oxygen-carbon bond fission and that with nitrogen-carbon bond fission. The analogous reaction is already known in the decomposition of orthoester[4] to form ester and ether. In the compound V, the decomposition with oxygen-carbon bond fission to form alkyl cation is considered to be more difficult than that with nitrogen-carbon bond to form nitrile or isonitrile cations shown in the above scheme. By direct deprotonation from V, nitrile and orthoester anions are formed. On the other hand, with the migration of phenyl group, the isonitrile cation is formed along with simultaneous formation of the orthoester anion. The former deprotonates to form isonitrile and the orthoester anion loses the alkoxyl anion by the shift of an electron pair and forms ethyl propionate. Further work on this rearrangement of aldoximes and ketoximes is now in progress and will be reported in a later paper.

It is worth while reconsider the above-discussed dehydration reactions carried out with carbodiimide, acetylenic ether and ketene acetal. It is known that these compounds react readily with water to form urea, ester, and ester and alcohol according to the Eqs. 7, 8 and 9, respectively.

$$R{-}N{=}C{=}N{-}R + H_2O \longrightarrow R{-}NHC(OH){=}N{-}R \longrightarrow RHNCONHR \quad (7)$$

$$HC{\equiv}C{-}OR + H_2O \longrightarrow CH_2{=}C(OH){-}OR \longrightarrow CH_3COOR \quad (8)$$

$$CH_2{=}C(OR)_2 + H_2O \longrightarrow CH_3C(OH){-}(OR)_2 \longrightarrow CH_3COOR + R{-}OH \quad (9)$$

Finding a compound reactive with water would accordingly provide a method of looking for a dehydrating agent. If compounds with carbon-carbon or carbon-nitrogen bond are considered, allene with a twinned double bond and nitrile with a triple bond may also be used as an effective dehydrating agent.

$$R{-}CH{=}C{=}CH{-}R + H_2O \longrightarrow RCH_2C(OH){=}CH{-}R \longrightarrow RCH_2COCH_2R \quad (10)$$

$$R{-}C{\equiv}N + H_2O \longrightarrow R{-}C(OH){=}NH \longrightarrow RCONH_2 \quad (11)$$

The hydration reactions of Eqs. 10 and 11 have already been studied[7,8]. These compounds may be added to the agents of the intramolecular dehydration reactions of the here-discussed type.

Experimental

Reaction of Phenylnitromethane with Di-*p*-tolylcarbodiimide.—To a solution of phenylnitromethane (6.1 g., 0.045 mol.) and di-*p*-tolylcarbodiimide (10 g., 0.045 mol.) in 25 ml. dry benzene were added 10 drops of triethylamine. Then the mixture was heated under reflux for 2.5 hr. and *sym*-di-*p*-tolylurea precipitated. It was filtered and washed with benzene and weighed 5.2 g., (48% of theoretical), m. p. 257~9°C. 3-Phenyl-4-*p*-tolyl-5-*p*-tolylimino-oxadiazole was separated as a white crystal on standing the filtrate overnight at room temperature. It was recrystallized from 95% ethanol, 1.5 g., (10% of theoretical), m. p. 171~2°C.

Found: C, 77.42; H, 5.57; N, 12.30. Calcd. for $C_{22}H_{19}ON_3$: C, 77.75; H, 5.56; N, 12.24%.

7) G. Gustavson and N. Demjanow, *J. prak. Chem.*, [2], **38**, 202 (1888).

8) J. J. Sudborough, *J. Chem. Soc.*, **67**, 601 (1895).

Reactions of Aldoximes with Di-*p*-tolylcarbodiimide.—A solution of α-benzaldoxime (4.4 g., 0.036 mol.) and di-*p*-tolylcarbodiimide (8 g., 0.036 mol.) in 35 ml. dry ether was heated under reflux for 11 hr. and *sym*-di-*p*-tolylurea precipitated. It was filtered and washed with ether and weighed 5.5 g., (63% of theoretical), m. p. 258~259°C. The filtrate was evaporated and distilled. Benzonitrile, b. p. 70~2°C (21 mmHg), 2.4 g., (65% of theoretical) was obtained. The same result was obtained when α-benzaldoxime and di-*p*-tolylcarbodiimide were reacted in the presence of tertiary alkyl amine.

When *n*-heptanaldoxime (4.7 g., 0.036 mol.) in place of α-benzaldoxime in the above experiment was used, di-*p*-tolylurea, 7.3 g., (67% of theoretical) and *n*-heptanneitrile, 2.3 g., (57% of theoretical) were obtained.

Reactions of Aldoximes with Dicyclohexylcarbodiimide.—To a solution of dicyclohexylcarbodiimide (10 g., 0.049 mol.) in 50 ml. dry benzene was added α-benzaldoxime (5.9 g., 0.049 mol.). Then the reaction started soon with the liberation of heat and *sym*-dicyclohexylurea began to precipitate. After the mixture was refluxed for 7 hr., it was cooled and filtered. The precipitate of *sym*-dicyclohexylurea was weighed 11 g., (92% of theoretical), m. p. 226~228°C. The filtrate was worked up in the usual manner, benzonitrile 5.1 g., (77% of theoretical), b. p. 83~84°C (21 mmHg), was obtained.

With *n*-heptanaldoxime (6.3 g., 0.049 mol.) in place of α-benzaldoxime in the above experiment, dicyclohexylurea 8.9 g., (81% of theoretical) and *n*-heptaennitrile 3.3 g., (62% of theoretical) were obtained.

Reaction of Phenylnitromethane with *n*-Butyl Acetylenic Ether.—To a solution of phenylnitromethane (2.8 g., 0.02 mol.) and *n*-butyl acetylenic ether (4.0 g., 0.04 mol.) in 10 ml. dry benzene were added 20 drops of triethylamine and the mixture was refluxed for 10 hr. After removing benzene and triethylamine in vacuo, *n*-butyl acetate 1.5 g., (32% of theoretical), b.p. 123~126°C and 3-phenyl-5-*n*-butoxyisoxazole 0.8 g., (18% of theoretical), b. p. 120~125°C (0.1 mmHg) were obtained. The latter solidified on cooling and melted at 59~61°C (recrystallized from ethanol-water).

Found: C, 71.8; H, 6.94; N, 6.63. Calcd. for $C_{13}H_{15}NO_2$: C, 71.8; H, 6.93; N, 6.46%.

The residual oil crystallized by the addition of 95% ethanol and melted at 209~210°C (recrystallized from 95% ethanol), (0.2 g.). It was 3,4,5-triphenylisoxazole.

Reaction of Benzaldoxime with Methyl Acetylenic Ether.—To a solution of α-benzaldoxime (6.1 g., 0.05 mol.) and methyl acetylenic ether (2.8 g., 0.05 mol.) in 10 ml. dry ether were added 20 drops of triethylamine and the mixture was allowed to stand for 43 hr. at room temperature. Then it was worked up in the usual manner, methyl acetate 1.5 g., (41% of theoretical), b. p. 57°C and benzonitrile 3.6 g., (69% of theoretical), b. p. 187~189°C, were obtained.

Reaction of α-Benzaldoxime with Methyl Ketene Diethyl Acetal in the Presence of Boron Trifluoride and Mercuric Oxide.—To a solution of methyl ketene diethyl acetal (3 g., 0.023 mol.) and α-benzaldoxime (2.8 g., 0.023 mol.) in 10 ml. dry ether were added 2 drops of boron trifluoride (40% ether solution) and 0.1 g. of mercuric oxide. After the mixture was refluxed for 6 hr., ether was removed and distilled. Ethyl propionate 0.8 g., (68% of theoretical), b. p. 45°C (108 mmHg), benzonitrile 0.9 g., (38% of theoretical), b.p. 57~59°C (4 mmHg), benzoisonitrile 0.5 g., (21% of theoretical), b. p. 38~42°C (3 mmHg), and ethyl orthopropionate 0.6 g., (30% of theoretical), b. p. 89°C (75 mmHg) were obtained.

Reaction of α-Benzaldoxime with Methyl Ketene Diethyl Acetal in the Presence of Triethylamine.—To a solution of methyl ketene diethyl acetal (3 g., 0.023 mol.) and α-benzaldoxime (2.8 g., 0.023 mol.) in 10 ml. dry ether was added 2 drops of triethylamine. After refluxing the mixture for 7 hr., it was worked up in the usual manner, the addition compound of α-benzaldoxime and methyl ketene diethyl acetal 4.8 g., (83% of theoretical), b. p. 157~158°C (18 mmHg), was obtained.

Found: C, 66.75; H, 8.25; N, 5.57. Calcd. for $C_{14}H_{21}NO_3$: C, 66.90; H, 8.42; N, 5.57%.

The same result was observed when α-benzaldoxime and methyl ketene diethyl acetal were reacted in the absence of catalyst.

Decomposition of the Addition Compound in the Presence of Boron Trifluoride and Mercuric Oxide.—To a solution of the above addition compound (2.5 g., 0.01 mol.) in 5 ml. dry ether were added 2 drops of boron trifluoride (40% ether solution) and 0.1 g. of mercuric oxide. After refluxing the mixture for 6 hr., it was treated in the usual manner and ethanol 0.1 g. (22% of theoretical), ethyl propionate 0.6 g. (59% of theoretical), b.p. 38°C (120 mmHg), benzonitrile 0.5 g. (40% of theoretical), b. p. 52°C (2 mmHg), and benzoisonitrile 0.6 g. (50%. of theoretical), b. p. 54°C (12 mmHg) were obtained.

Decomposition of the Addition Compound in the Presence of Boron Trifluoride.—With 2 drops of boron trifluoride (40% ether solution) in place of the said two catalysts in the above experiment, ethanol 0.1 g. (22% of theoretical), ethyl propionate 0.5 g. (49% of theoretical), b. p. 42°C (96 mmHg) and benzonitrile 0.5 g. (41% of theoretical), b. p. 68.5°C (10 mmHg) were obtained.

Decomposition reaction of the addition compound in the presence of mercuric oxide could not be observed and the starting material was recovered.

Reaction of *n*-Heptanaldoxime with Methyl Ketene Diethyl Acetal in the Presence of Boron Trifluoride and Mercuric Oxide.—To a solution of *n*-heptanaldoxime (2.8 g., 0.022 mol.) and methyl ketene diethyl acetal (2.8 g., 0.022 mol.) in 10 ml. dry ether were added 2 drops of boron trifluoride (40% ether solution) and 0.1 g. of mercuric oxide. After the mixture was refluxed for 7 hr., it was treated in the usual manner and ethanol 0.7 g. (78% of theoretical), ethyl propionate 0.2 g. (10% of theoretical), b. p. 44~47°C (89 mmHg) and *n*-heptanitrile 1.3 g. (54% of theoretical), b. p. 67~67.5°C (13 mmHg) were obtained.

The authors wish to express their hearty thanks to Professor Toshio Hoshino for his encouragement and to Mr. Norio Shibata

for his help throughout the course of this experiment. Thanks are also due to Mr. Asaji Kondo for the microanalyses.

Department of Chemistry
Tokyo Institute Technology
Meguro-ku, Tokyo

On Solvolysis of α-Phosphorus(V) Oxide

By Masako SHIMA, Kazue HAMAMOTO* and Seiichiro UTSUMI

(Received April 11, 1960)

It has been well-known[1-3] since 1940 that phosphorus(V) oxide exists in three crystalline modifications (α, β, γ)[4] and that the crystal of the α-modification is composed of P_4O_{10} molecules in which four phosphorus atoms are at the apices of a tetrahedron and are bonded to one another with six P–O–P linkages[1,2,5], as is shown in Fig. 1. Water reacts violently

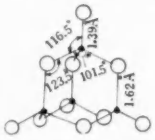


Fig. 1. The structure of the molecule P_4O_{10}.
○ Oxygen atoms • Phosphorus atoms

with it, and organic solvents such as alcohols and acetone[6] also indicate some chemical action. As regards the reaction process of α-phosphorus(V) oxide with water and the resulting products thereof, much information is available[7-11], but little is known about the reactions with organic solvents.

The present authors attempted to clarify the general reaction mechaniem of α-phosphorus (V) oxide to which special attention was given to the solvolytic opening of the P–O–P linkages in this molecule and the accompanying condensation processes of phosphate radicals. Experiments were conducted along three lines: (a) direct hydrolysis with a large quantity of pure water, (b) solvolysis with organic solvents (e.g. ethanol and acetone) which are miscible with water and have some reaction with the oxide and (c) hydrolysis of the oxide dispersed in organic solvents which are non-reactive and able to hold a limited amount of water.

Experimental

Materials.—Purification by subliming guaranteed reagent of α-phosphorus(V) oxide with simple

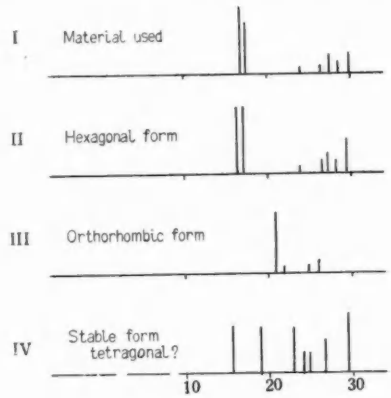


Fig. 2. The experimental X-ray diagram (I) of reagent α-phosphorus(V) oxide compared with those data (II~IV) of polymorphic forms of phosphorus oxide by Hill et al.[2].
Experimental conditions:
Cu K_α (Ni filter)
35 KVP—15 mA
Slit 0.2-2$^1/_2$-2$^1/_2$, 16-1-2
Scan. sp. 4°/min.
Ch. sp. 1 cm./min.

* Present address, Japan Atomic Energy Research Institute, Tokai, Ibaraki-ken.

1) H. C. J. deDeker and C. H. MacGillavry, *Rec. trav. chim.*, **60**, 153 (1941); H. C. J. deDeker, ibid., 413.
2) W. L. Hill, G. T. Faust and S. B. Hendricks, *J. Am. Chem. Soc.*, **65**, 794 (1943).
3) C. H. MacGillavry, H. C. J. deDeker and L. M. Nijland, *Nature*, **164**, 448 (1949).
4) The three crystalline modifications of phosphorus-(V) oxide were designated by deDeker et al. as S_1, S_2 and S_3, and by Thilo et al., as M., R. and S.
5) G. C. Hampson and A. J. Stosick, *J. Am. Chem. Soc.*, **60**, 1814 (1938).
6) T. Kuwata, "Yozai", Maruzen Co. (1951), p. 256.
7) R. N. Bell, L. F. Audrieth and O. F. Hill, *Ind. Eng. Chem., Anal. Ed.*, **44**, 568 (1952).
8) E. Thilo and W. Widker, *Z. anorg. allgem. Chem.*, **277**, 27 (1954).
9) A. E. R. Westman, A. E. Scott and J. T. Pedley, *Chemistry in Canada*, Oct. 1 (1952).
10) A. Travers and Yu Kwong Chu, *Compt. rend.*, **198**, 2169 (1934).
11) S. Glixelli and K. Borantynsky, *Z. anorg. allgem. Chem.*, **235**, 225 (1938).

equipment proved to be unsuitable because of the extraordinarily strong absorptive power of the sublimate against traces of moisture remaining in dried vessels. However, as this material was confirmed to be very pure by X-ray examination (as shown in Fig. 2) it was used without further purification.

Organic Solvents. — Diethyl ether and benzene were dried with sodium metal, acetone with anhydrous sodium sulfate and ethanol with calcium oxide. The diethyl ether, benzene and acetone were of reagent grade and ethanol was of guaranteed grade. They were distilled at least twice and used dry or after a definite weight or volume of water had been added.

Reaction Procedure.—Each solvent was weighed in a beaker or in a large weighing bottle[12], kept at 0°C and agitated vigorously with a magnetic stirrer. Then 0.5 g. of α-phosphorus(V) oxide was added to the solvent in small portions using a special vessel equipped with a closely fitting lid worked by a spring so as to cause complete dispersion[13].

When water or any solvent miscible with water, for example, acetone or ethanol with or without added water, was used, stirring was continued until the added oxide thoroughly dissolved, the resulting solution was still kept at 0°C and neutralized with 1 N sodium hydroxide[14] (indicator; litmus test paper). In the case of pure water 10 ml. was used each time. Since α-phosphorus(V) oxide went almost completely into solution[15], no treatment was necessary before spotting 0.01 ml. or 0.02 ml. of the sample with a micropipette on a chromatographic paper along a starting line. Different species of the condensed phosphates in this solution were successfully separated. At the same time, a 2 ml. aliquot of the sample solution was taken in order to determine the total phosphorus-(V) concentration by colorimetric analysis. In the case of acetone or ethanol with or without added water (20 ml. in total volume), α-phosphorus(V) oxide dissolved only to a limited extent, and the remaining precipitate had to be separated from the solution with decantation and dissolved in 20 ml. of pure water. After the volume had been adjusted, the contents of the various condensed phosphates, and the total phosphate concentration were determined for these two solutions. On the other hand, in the case of diethyl ether (13 ml.) or benzene (10 ml.), α-phosphorus(V) oxide was dispersed in it as perfectly as possible, and, the mixture being kept in vigorous agitation with a magnetic stirrer, 10 ml. of water was added, and the resulting solution was neutralized with 1 N sodium hydroxide, and then transferred to a separating funnel. The organic phase was removed from the aqueous phase and washed with 2 ml. of water; it was discarded, for no trace of phosphorus(V) was found in it. The aqueous phase was added to the above wash water, and was subjected to analysis for the various condensed phosphates and the total phosphate concentration.

The Separation of Various Species of Condensed Phosphates by Filter Paper Chromatography.— Various condensed phosphates differing in degree and mode of polymerization were separated by ascending chromatography on filter paper. The method has been studied by many workers[9,16-21]. In the present work, eleven kinds of acidic solvent and six kinds of basic solvent already reported were tested with Toyo Roshi No. 5B for quantitative analysis[22], and the two following solvents were chosen for their most effective separating ability. Acidic solvent: a mixture of propan-2-ol (70 ml.), water (30 ml.), trichloroacetic acid (5 g.) and concentrated aqueous ammonia (0.3 ml.). Basic solvent: a mixture of isobutanol (30 ml.), ethanol (30 ml.), water (39 ml.) and concentrated aqueous ammonia (1 ml.). R_f values are given in Table I. For further work, experimental conditions were made as follows; length of the filter paper, 40 cm.; width, 2.5 cm.; time of chromatographic development, about 20 hr.; temperature, 10~20°C (room temperature). Lower ends of filter papers were narrowed after the method of Thilo et al.[19a]. The chromatographic separation seemed to improved by this cutting. Each condensed phosphate distributed in bands on a chromatogram was identified by Crowther's method[17c].

Colorimetric Estimation of Each Condensed Phosphate. — The condensed phosphates separated in bands on each chromatogram were determined by Crowther's method[17c] by the following procedure. Bands were cut out, soaked with 10 ml. of 1 N aqueous ammonia and eluted by warming on a

12) When dry or volatile solvent was used, reaction was performed in a large weighing bottle with a fitted stopper to prevent moist air from entering or the solvent from evaporating.

13) α-Phosphorus(V) oxide must be kept moisture-tight during the operation. The above-mentioned vessel, originally designed as a receptacle of "Ajinomoto powder", was obtained from the Ajinomoto Co., and was found to be very suitable for this purpose.

14) In the case of solvolysis with a large amount of water, the resulting solution was almost clear. This solution was subjected to moderate neutralization with Amberlite IRC-50, Na-form resin, or with sodium carbonate, so that the hydrolysis that might otherwise proceed during this procedure could be prevented. But these three neutralizing procedures with respective agents did not show any difference in results, as is shown in Table II.

15) A slight turbidity may appear in the solution, but it can be dispersed uniformly in a colloidal form and made to disappear when the solution is stirred sufficiently.

16) a) J. P. Ebel and Y. Volmar, *Compt. rend.*, **233**, 415 (1951); b) Y. Volmar, J. P. Ebel and Y. F. Bassili, *Bull. soc. chim. France*, **20**, 1085 (1953); c) J. P. Ebel, ibid., 991; d) 998; e) 1089; f) 1096.

17) a) A. E. R. Westman and A. E. Scott, *Nature*, **168**, 740 (1951); b) A. E. R. Westman and J. Crowther, *J. Am. Cer. Soc.*, **37**, 420 (1954); c) J. Crowther, *Anal. Chem.*, **26**, 1383 (1954).

18) a) H. Grunze and E. Thilo, *Mathematik allgem. Naturwiss.*, **1953**, No. 5, 1 (1953); b) H. Roux, E. Thilo, H. Grunze and M. Viscontini, *Helv. Chim. Acta*, **38**, 15 (1955); c) H. Grunze and E. Thilo, *Z. Silikattechnik*, **7**, 134 (1956).

19) E. Karl-Kroupa, *Anal. Chem.*, **28**, 1091 (1956).

20) A. L. Huhti and P. A. Gartaganis, *Can. J. Chem.*, **34**, 785 (1956).

21) G. G. Berg, *Anal. Chem.*, **30**, 213 (1958).

22) Filter papers often contain phosphorus(V) which can be detected by a qualitative method or with colorimetric analysis of eluted solution. Toyo Roshi No. 52 for chromatography contains substances which reduce ammonium molybdate during the procedure of phosphorus(V) detection. In Toyo Roshi No. 53 or No. 54 for chromatography, this was not noticed, but by the use of No. 54 paper, separation of various species of condensed phosphates was notably poor. In this work, No. 53 paper was also used.

TABLE I. SEPARATION OF VARIOUS CONDENSED PHOSPHATES BY ASCENDING CHROMATOGRAPHY WITH THE USE OF TWO KINDS OF SOLVENT

Filter paper; TOYO ROSHI No. 5B for quantitative analysis.

Solvents	pH	Distances from base to front cm.	Time of development hr.	R_f						Reference
				Ortho-	Pyro-	Tripoly-	Trimeta-	Tetra-meta-	Highpoly-	
Acidic	1.65	20.6	9.67	0.75	0.52	0.38	0.26	0.12	0	18b, 20
Basic	11.35	19.2	8.5	0.37	0.28	0.25	0.59	0.47	0	18b

* All phosphates were used in the form of sodium salts. Standard substances were sodium salts. Test samples were neutralized with sodium hydroxide, sodium carbonate or sodium-form resin. But as the hydrogen ion concentration of chromatographic solvents was adjusted with aqueous ammonia, sodium may have been replaced by ammonium during the development process. In our experiments, the appearance of a spot of another phosphate species was very often noticed, especially in a basic solvent. This additional spot was confirmed to correspond to amomnium salt, for when the sodium in the phosphate had been replaced by ammonium through ion exchange resin column of Amberlite IR-120 ammonium-form, this spot alone was observed.

** The composition of the solvents are described in the text.

TABLE II. DISTRIBUTION OF PHOSPHORUS AMONG THE SOLVOLYSIS PRODUCT OF PHOSPHORUS(V) OXIDE BY A LARGE AMOUNT OF ICE WATER

No.	Neutralizing agent	PO_4^{3-}	$P_2O_7^{4-}$	$P_3O_{10}^{5-}$	$(PO_3)_3^{3-}$	$(PO_3)_4^{4-}$	Highpoly	Chromatographic solvent
1	NaOH	2.0	2.1	2.7	14.1	60.1	19.0	Acidic
2	Na_2CO_3	1.5	1.8	2.2	12.9	48.0	33.7	Acidic
3	Resin		7.1		15.2	60.2	17.4	Acidic
4	Resin		26.7***			64.5	8.9***	Basic
5	Resin	2.0	1.5	4.6	16.0	66.0	10.3	Acidic
6	Resin	2.2	3.5***	9.1***	14.0	66.0	6.0***	Basic
(Average of the above 2 lines)		2.1	2.5	6.8	15.0	66.0	8.2	
7	NaOH	2.3	1.5	4.5	12.9	61.3	17.4	Acidic
8	NaOH	2.6	2.0	2.3	16.2	58.5	18.3	Acidic
(Total average)		2.1	2.1	4.2	14.5	60.0	16.4	

* Data from No. 5 to No. 8: Average of two determinations.

** Figures in this Table are the values of percentage distribution of phosphorus among respective phosphates.

*** During separation by filter paper chromatography, hydrolysis of the condensed phosphates seemed to advance more by the use of basic solvent than by the use of the acidic solvent. Accordingly, use of the basic solvent was avoided except in the experiment with a large amount of water.

water bath for 1 hr. The eluted sample solutions were treated with the molybdenum reagent in the ordinary way. The absorbance due to molybdenum blue was measured by a Hitachi EPU-2A type spectrophotometer at 830 mμ in glass cells with a 1 cm. light path using distilled water as the reference.

Results

Solvolysis (or Direct Hydrolysis) by a Large Quantity of Water.—The main product in this case was tetrametaphosphoric acid mounting up to ca. 60% of phosphorus in agreement with the results of Bell et al.[7], Thilo et al.[8] and Westman et al.[9]. The detailed numerical records of contents of each condensed phosphate produced by this direct action are given in Table II.

Solvolysis by Acetone.—The ratio of acetone to water was varied as follows: 10:0, 9.5:0.5, 9.0:1.0, 5.0:5.0, 0:10 by volume. The solvolysis by pure acetone gave 28.5% of tetrametaphosphoric acid and 42% of highpolyphosphoric acid as the major product. The percentage of tetrametaphosphoric acid increased with the water content of the solvent. The results are illustrated in Fig. 3.

Solvolysis by Ethanol.—The ratio of ethanol to water was varied in the same way as for acetone and water. *a*-Phosphorus(V) oxide reacted with anhydrous ethanol and most of phosphorus(V) changed into pyrophosphoric acid, less than 5% of it becoming highpolyphosphoric acid and none turning into tetrametaphosphoric acid. Up to 50% of water

TABLE III. DISTRIBUTION OF PHOSPHORUS AMONG THE HYDROLYSIS PRODUCT OF PHOSPHORUS(V) OXIDE WITH ETHYL ETHER AND BENZENE AS DISPERSING AGENT

P_4O_{10} : H_2O	Dispersing agent	PO_4^{3-}	$P_2O_7^{4-}$	$P_3O_{10}^{5-}$	$(PO_3)_3^{3-}$	$(PO_3)_4^{4-}$	Highpoly	Number of highpoly spot
Dehydrated	Ether	1.76	1.02	0	14.4	68.3	14.4	2
1 : 2	Ether	2.42	2.42	0	12.4	50.3	32.2	2
1 : 10	Ether	1.88	1.07	3.44	10.2	55.3	28.9	3
Dehydrated	Benzene	1.56	0.96	1.66	11.4	65.7	18.6	2
1 : 1	Benzene	2.06	1.13	1.68	10.6	57.5	27.1	1
1 : 2	Benzene	1.93	0.99	1.86	11.4	58.5	25.6	1

* Data with ether: Average of four determinations.
Data with benzene: Average of two determinations.

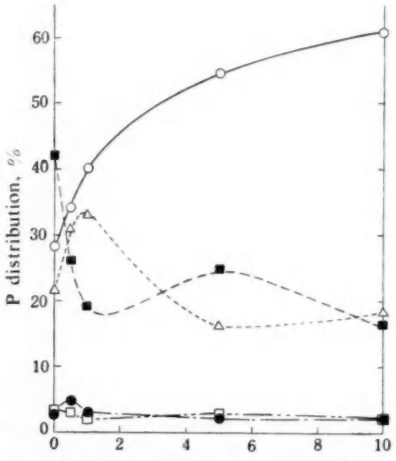


Fig. 3. Distribution of phosphorus among the solvolysis product of phosphorus(V) oxide by acetone and water-in-acetone system as solvent.
● Orthophosphate
□ Pyrophosphate
△ Tripoly- and trimetaphosphates
○ Tetrametaphosphate
■ Highpolyphosphate

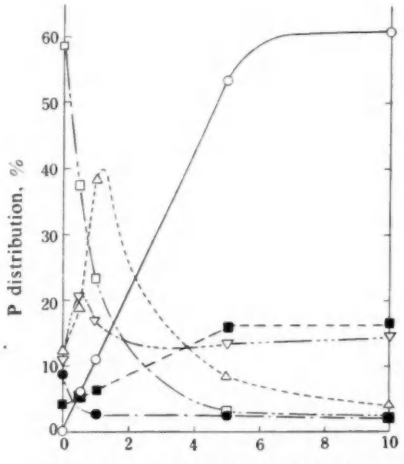


Fig. 4. Distribution of phosphorus among the solvolysis product of phosphorus(V) oxide by ethanol and water-in-ethanol system as solvent.
● Orthophosphate
□ Pyrophosphate
△ Tripolyphosphate
▽ Trimetaphosphate
○ Tetrametaphosphate
■ Highpolyphosphate

content, the yield of tetrameta- and highpolyphosphoric acid is linerly related to the water content, the yield of pyrophosphoric acid being rapidly decreased with increase in water content. The entire result is shown in Fig. 4.

Hydrolysis with Diethyl Ether and Benzene as Dispersing Agents.—It was considered that when these solvents were used in a completely anhydrous state, results might differ essentially from what would be the case when they contained initially a minute amount of water. However, results did not show the expected tendency distinctly, as may be seen in Table III.

Discussion

The molecular structure of α-phosphorus(V) oxide can be conveniently represented by a square formula I in Fig. 5, in which four P=O bonds are at the four corners and six P-O-P linkages are shown by four sides and two diagonals.

The P=O bonds are very stable as indicated by the short distances shown in Fig. 1, and they remain unaffected throughout the reactions dealt with in this study. Only the P-O-P linkages are attacked by reactive solvent molecules. Reaction of α-phosphorus(V) oxide

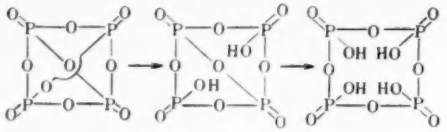


Fig. 5. Formulation of the process of tetrametaphosphoric acid formation.

with a large quantity of water, yielding tetrametaphosphoric acid as a principal product, can be formulated as shown in Fig. 5. The first water molecule approaching the oxide molecule opens any one of the six P–O–P linkages and produces an intermediate hydrolyzate (II), which is attacked by the second water molecule in succession. The fact that the main product is III can be explained by assuming that the weakest P–O–P linkage in II is the one situated diagonally opposite. This is quite easy to understand because only this P–O–P linkage is left to be strained owing to the bond angles of phosphorus atoms. Moreover, as the molecule of tetrametaphosphoric acid (III) has a fairly symmetrical structure, it is sufficiently stable and resists further attack of water molecules; it can be detected practically intact after the hydrolysis experiment. When the oxide reacts with alcohol, reaction proceeds I–IV–V–VI as shown in Fig. 6, yielding pyrophosphoric acid by the hydrolysis of the rather unstable ester formed. The reason why V receives further attack is attributable to its asymmetrical structure.

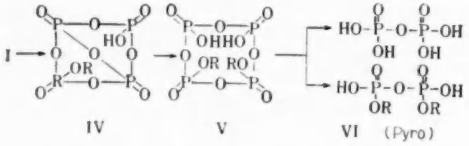


Fig. 6. Formulation of the process of pyrophosphoric acid formation.

A small quantity of trimeta- and tripolyphosphoric acids together with a still smaller quantity of orthophosphoric acid appearing in this case is explained as owing to the simultaneous reaction occurring along the schemes shown in Fig. 7. The reason why this branch reaction is possible in the case of alcoholic solvolysis must lie in the fact that the weak linkages in the intermediate IV are not restricted to the one diagonally opposite, because the ethyl radical is very large as compared with hydrogen atom and does not become ionized while hydrogen does. Other P–O–P linkages

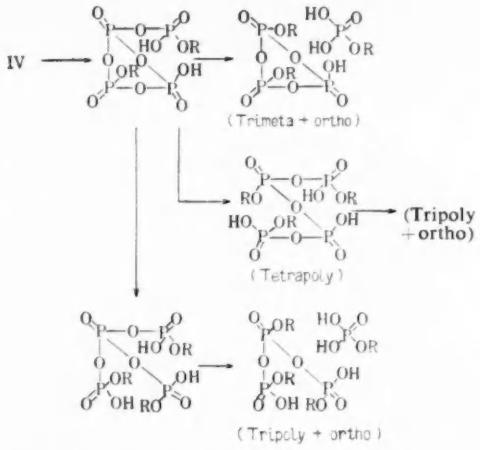


Fig. 7. Formulation of the process of tripoly-, tetrapoly- and orthophosphoric acid formation.

represented by sides of the square in IV may rupture though to a less extent. The phosphorus atom quota found in trimeta- and tripolyphosphoric acids and that found in orthophosphoric acid are in the ratio of three to one, which is quite consistent with the above-mentioned postulation.

When alcohol mixed with a small quantity of water is the reacting solvent against the oxide, tripoly- and trimetaphosphoric acids appear in a conspicuous amount in place of pyrophosphoric acid. As the water content further increases, these tri- species are very rapidly replaced by tetrametaphosphoric acid. It must, however, be noted that the above-mentioned transient increase in tripoly- and trimetaphosphoric acid is not accompanied by the production of a corresponding amount of orthophosphoric acid.

The branch reaction mentioned above does not explain the missing of orthophosphoric acid in this case, and for that same reason, it can explain the increase neither in tripoly- nor in trimetaphosphoric acid. These tri-species can not originate from highpolyphosphoric acid as precursor, because the production of the latter increases only gradually and without a maximum with the increase of water content in the solvent.

Involvement of condensation mechanism of phosphate radicals is the only conceivable explanation for the above. Condensation of phosphate radicals is an endothermic reaction, and does not occur under usual conditions in solution. It is here postulated that it does occur when a solvolytic opening of the P–O–P

linkages gives rise to the excitation of phosphate radicals and when they are close to one another. The same argument will explain the ever increasing formation of highpolyphosphoric acid in hydrolysis. The maximum yield of tripoly- and trimetaphosphoric acid with 90% ethanol may be attributable to the condensation between a pyrophosphoric acid radical and free orthophosphate radical.

Vigorous reaction between the oxide and water evolves much heat, and even under a cooling condition, some local heating can not be avoided. This must undoubtedly promote the condensation process.

Thorough dispersion of the oxide in dry ether or benzene was attempted to ensure synchronized contact with a large amount of water. Similar experiments, using ether and benzene containing trace quantities of water were carried out as well. In the former case, one would expect complete transformation to 100% tetrametaphosphoric acid, whereas in the latter case, one would expect 100% highpolyphosphoric acid. Difficulty in pulverizing the oxide crystals and the reacted mass prevented us from obtaining clear-cut results, but the expected tendency was observed.

Acetone may behave as a solvent having -OH radicals, as is explicable by its enol form, forming $-P-O-C\begin{matrix}CH_3\\CH_2\end{matrix}$ on solvolytic opening of a P-O-P linkage. This must be an intermediate very liable to undergo subsequent decomposition giving rise to a fairly large amount of highpolyphosphoric acid as the final hydrolysis product. Tetrametaphosphoric acid can be detected right from the beginning of the reaction, as well as tripoly- and trimetaphosphoric acid. In this case too, almost no orthophosphoric acid is produced.

Orthophosphoric acid is the most easily detectable species among various phosphates; it is inconceivable for us to have missed it in the analysis.

Summary

1. α-Phosphorus(V) oxide was allowed to react with water, with ethanol or acetone, both dry or mixed with water by adding the powder crystal directly into these liquids. The oxide was also brought in contact with water after being dispersed in diethyl ether or benzene mechanically.

2. The main final hydrolysis products formed in the following cases were tetrametaphosphoric acid by direct action of a large quantity of water, pyrophosphoric acid by anhydrous ethanol, tripolyphosphoric acid by ethanol with a low water content, and highpolyphosphoric acid by anhydrous acetone. Quick contact with water after the oxide has been dispersed in ether or benzene leads to the formation of a larger amount of tetrametaphosphoric acid when these solvents were dry, while the formation of an increased amount of highpolyphosphoric acid was the result when they contained trace quantities of water initially.

3. Separation, identification and estimation of various condensed phosphate species were executed by paper chromatography and colorimetric analysis.

4. Reaction mechanisms were postulated to explain these results. Special attention was given to the solvolytic opening of P-O-P linkages and the accompanying condensation process of phosphate radicals.

Department of Chemistry
Faculty of Science
Ochanomizu University
Otsuka, Tokyo

Untersuchungen über Meso-ionischen Verbindungen. XI. Versuche zur Darstellung von 3-(2'-Pyridyl)sydnon

Von Masaki OHTA und Mitsuo MASAKI

(Eingegangen am 11. März, 1960)

In der X. Mitteilung[1] dieser Reihe wurde gezeigt, daß bei der Einwirkung von Bisulfitverbindungen der Aldehyde und Alkalicyanid auf 3-Aminopyridin α-substituierte 3-Pyridylglycinnitrile bzw. 3-Pyridylglycinnitril selbst entstehen, und daß diese Nitrile sich durch Hydrolyse in die entsprechenden Glycine umsetzen, die weiter bei der Einwirkung von Natriumnitrit in *N*-Nitrosokörper umgewandelt werden und aus den letzteren 4-substituierte 3-(3'-Pyridyl) sydnone durch Cyclisierung-Reaktion mit Essigsäureanhydrid dargestellt werden können.

Nach dieser Methode haben wir eine Reihe von Untersuchungen ausgeführt, die das Ziel hatten, 2-Pyridylglycin, 3-(2'-Pyridyl)sydnon und dessen derivate darzustellen.

Schon ist von Bristow u. a.[2] die Darstellung von 2-Pyridylglycinnitril nach der oben erwähnten Methode berichtet worden. Andererseits wurde von Reynaud u. a.[3] beschrieben, daß sie nach dieser Methode nur ein dunkelfarbiges Produkt und kein Nitril erharten konnten. Sie erhielten dabei das Nitril durch einen anderen Weg, nähmlich bei der Einwirkung von Bromdiäthylacetal auf 2-Aminopyridin in der Gegenwart von Natriumamid erhielten sie Pyridylaminodiäthylacetal, das durch Hydrolyse in das entsprechende Aldehyd umgewandelt wurde, dessen Oxim beim Versetzen mit Essigsäureanhydrid den *N*-Acetylkör per des Nitrils lieferte.

Durch die Einwirkung von Bisulfitverbindung des Formaldehyds und Natriumcyanid auf 2-Aminopyridin erhalten wir das Nitril (I), das durch Kochen mit Salzsäure salzsaures *N*-(2-Pyridyl)glycin[3](II) ergibt.

Bei der Einwirkung von Natriumnitrit auf II in Kälte, entsteht eine kristalline Substanz von Schmp. 119°C, die nicht *N*-Nitroso-*N*-(2-pyridyl)glycin (III), sondern α-Nitroso-*N*-(2-pyridyl)glycin (IV) ist, dessen Konstitution durch Elementaranalyse und durch Reaction mit Essigsäureanhydrid festgestellt wurde.

Wenn man die Nitrosoverbindung in Essigsäureanhydrid löst und bei Raumtemperatur stehen läßt, so fällt langsam der farblose Niederschlag vom Schmp. 196~8°C aus, dessen Molekularformel, $C_7H_6O_3N_2$, durch Elementaranalyse festgestellt wurde. Unsere Vermutung, daß dieses Produkt *N*-(2-Pyridyl)-oxamidsäure (V) sei, wurde durch IR-Absorptionen bei 1300, 1540 und 1655 cm^{-1} als dem sekundären Amid typische Banden und durch die Bildung von *N*, *N'*-Di-(2-pyridyl)oxamid (VII) bei der Pyrolyse bestätigt.

Beim Erhitzen auf 200~220°C ergibt V in guter Ausbeute VII, das durch die Mischprobe mit dem authentischen[4] Präparat bestätigt wurde. Laurent u. a.[5] beobachteten beim Erhitzen von Oxanilsäure auf höheren Temperaturen die Bildung von Oxanilid. Man kann sich die Bildung von VII aus V so denken, daß zunächst aus V durch Pyrolyse 2-Aminopyridin entsteht, und das letztere durch weitere Einwirkung von V in VII umgewandelt wird. In der Tat kann man Aminopyridiniumsalz vom V als Zwischenverbindung erhalten.

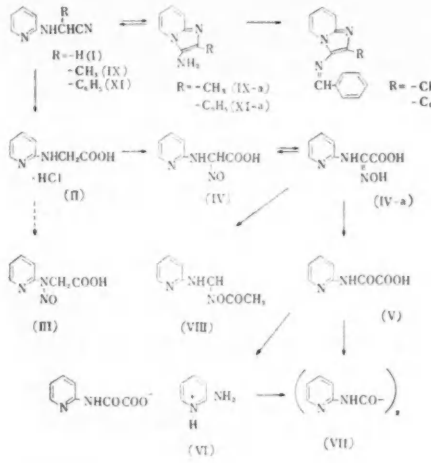
Wenn man IV mit Essigsäureanhydrid erhitzt, so erhält man *N*-(2-Pyridyl)acetylformamidoxim (VIII), dessen Bildung man sich so vorstellen kann, daß zunächst in der tautomeren Form (IV-a) des IV Acetylierung erfolgt, darauf dieses sich unter Decarboxylierung in VIII überführen läßt.

Wie oben erwähnt, ist die bei Nitrosierung auf 2-Pyridylglycin erhaltene Verbindung nicht *N*-Nitroso- (III), sondern α-Nitroso-körper (IV), so versuchten wir die substituierten 2-Pyridylglycine, die CH_3- oder C_6H_5- Gruppe am α-Kohlenstoffatom tragen, darzustellen, um *N*-Nitroso-(2-pyridyl)glycin zu erhalten, das durch Cyclisierung 3-(2'-Pyridyl)sydnon ergeben sollte.

Im Wasser reagiert 2-Aminopyridin mit Bisulfitverbindung des Acetaldehyds oder des Benzaldehyds und Natrium cyanid, wobei α-(2-Pyridylamino)propionitril (IX) oder α-(2-Pyridylamino)phenylacetnitril (XI) entsteht.

Unter verschiedenen Bedingungen versuchten wir die Hydrolyse des XI, doch konnten wir kein entsprechendes Glycin erhalten, z. B. beim Erhitzen von XI mit Mineralsäuren entsteht

1) M. Ohta und M. Masaki, Dieses Bulletin, 33, 649 (1960).
2) N. W. Bristow, P. T. Charlton, D. A. Peak und W. F. Short, *J. Chem. Soc.*, **1954**, 616.
3) P. Reynaud, T. Tupin und R. Delaby, *Bull. soc. chim.*, **1957**, 718.
4) A. E. Tschitschibabin, *Ber.*, **57**, 1172 (1924).
5) A. Laurent und C. Gerhardt, *Ann.*, **68**, 20 (1848).



nur sein stabiles Salz. Diese Tatsache scheint zu zeigen, daß bei XI Ringschluß eintritt[2] und ein Imidazol-Kern sich bildet, nähmlich, XI befindet sich in der tautomeren Form (XI-a). In der Tat läßt sich XI mit Benzaldehyd in nah-quantitativer Ausbeute in Benzal-Derivat (XII) überführen.

Es gelang uns auch nicht aus IX das entsprechende Glycin darzustellen. In ähnlicher Weise ergibt IX bei Einwirkung von Benzaldehyd Benzal-Derivat (X) in guter Ausbeute.

Beschreibung der Versuche

2-Pyridylaminoacetnitril (I).—Man versetzt 4.1 g von 37 proz. Formalin mit einer Lösung von 5.4 g Natriumbisulfit in 8 ccm Wasser, erhitzt 0.5 Std und versetzt daraufhin mit 4.7 g 2-Aminopyridin. Nach ein stdg. Erhitzen und Umrühren setzt man 5 g Natriumcyanid in wenigem Wasser zu. Das Gemisch wird unter mechanischem Rühren noch 4 Std auf dem siedendem Wasserbad erwärmt, und der ausgefallene Niederschlag abfiltriert. Das Filtrat schüttelt man 5 mal mit je 30~50 ccm Chloroform aus. Das vereinigte Chloroformextract wird mit Natriumsulfat getrocknet und im Vakuum eingedampft. Es hinterbleibt schwarzes Öl, wozu 30~40 ccm Äther hinzugefügt wird und läßt es stehen. Dabei fallen braune Prismen aus. Ausbeute 2~3 g (30~45%). Schmp. 126~7°C (aus Benzol).

Salzsaures 2-Pyridylglycin (II).—Man löst 2.1 g I in 20 proz. Salzsäure, erhitzt 3~4 Std auf dem Wasserbad und dampft das Reaktionsgemisch im Vakuum ein. Der Rückstand wird mit Äthanol ausgezogen, die Lösung mit Aceton versetzt und bei Raumtemperatur stehen gelassen. Dabei fallen farblose Kristalle aus. Ausbeute 2.7 g (70%). Schmp. 206°C (aus Äthanol).

Gef.: N 14.71. Ber. für $C_7H_9O_2N_2Cl$: N 14.85.

Pikrat. Gelbliche Nadeln vom Schmp. 199°C (aus Methanol)

Gef.: N 18.59. Ber. für $C_{13}H_{11}O_9N_5$: N 18.37.

α-Nitroso-(2-pyridyl)glycin (IV).—Man löst 1.9 g II in 20 ccm Wasser und fügt 0.7 g Natriumnitrit unter Eiskühlung hinzu, wobei sich langsam ein farbloser Niederschlag abscheidet. Nach 3~4 std. Stehen unter Eiskühlung wird er abfiltriert. Ausbeute 1.5 g. Gelbliche Nadeln vom Schmp. 119°C (aus Wasser).

Gef.: C 46.61; H 3.90; N 23.20. Ber. für $C_7H_7O_3N_3$: C 46.31; H 4.02; N 23.32.

Diese Subtanz zeigt Liebermannsche Reaktion.

***N*-(2-Pyridyl)oxamidsäure (V).**—Man löst 1 g IV in 35 ccm Essigsäureanhydrid auf, wobei fast augenblicklich Farbumschlag von grün nach gelb erfolgt, und läßt dies bei Raumtemperatur stehen. Bald fing sich ein farbloser amorpher Niederschlag auszuscheiden an. Nach eintägigem Stehen wird der Niederschlag abfiltriert, und das Filtrat läßt sich bei Raumtemperatur untergehalten. Nach noch zwei Tagen filtriert man den aufs neue abgeschiedenen Niederschlag ab, der zusammen mit dem oben erhaltenen Produkt umkristallisiert wird. Farblose Naldeln vom Schmp. 196~8°C (aus Äthanol oder Essigsäure). Ausbeute 0.8 g (87%).

Gef.: C 50.71; H 4.13; N 16.95. Ber. für $C_7H_6O_3N_2$: C 50.60; H 3.61; N 16.87.

IR-Spektrum in KBr: 1300, 1540 und 1655 cm^{-1} (-NHCO-).

***N*,*N'*-Di-(2-pyridyl)oxamid (VII).**—Beim Erhitzen auf 200~220°C in Ölbad schmilzt V unter heftiger Zersetzung, und nach 2~3 min. Erhitzen wird das erhaltene, ölige Produkt abgekühlt, das bald kristallinish erstarrt Aus äthanol umkristallisiert, farblose Nadeln oder Prismen zeigen den Schmp. 161°C.

Gef.: C 59.30; H 4.19; N 23.19. Ber. für $C_{12}H_{10}N_4O_2$: C 59.50; H 4.16; N 23.13.

Mischprobe mit dem authentischen[4] Präparat zeigt keine Depresion.

***N*-(2-Pyridyl)oxamidsäure-Aminopyridiniumsalz (VI).**—Man erhitzt V in einem Kolben im Ölbad vorsichtig auf 200~210°C, und wenn V unter der Zersetzung kaum anfängt zu schmelzen, da kühlt man den Kolben ab. Bald erstarrt die erhaltene, ölige Substanz kristallinisch. Aus Äthanol umkristallisiert, erzeugen sich grünliche Blättchen vom Schmp. 206°C.

Gef.: C 55.08; H 4.98; N 21.40. Ber. für $C_{12}H_{12}O_3N_4$: C 55.39; H 4.62; N 21.54.

Die Substanz läßt sich durch nochmaliges Erhitzen unter Wasserabspaltung in VII umwandeln.

***N*-(2-Pyridyl)acetylfomamidoxim (VIII).**—Man löst 2 g IV in 25 ccm Essigsäureanhydrid und erhitzt auf siedendem Wasserbad. Nach einer Stunde wird die schwarze Lösung in N_2 unter vermindertem Druck eingedampft. Es hinterbleibt ein braunrotes Öl, das mit Äther ausgeschüttelt wird. Die ätherische Lösung wird mit Natriumsulfat getrocknet und eingeengt, wobei ein roter Rückstand erhalten wird, der aus Benzol umkristallisiert wird. Ausbeute 0.2 g. Bräunliche Nadeln vom Schmp. 192~5°C.

Gef.: C 53.87; H 5.15; N 23.50. Ber. für $C_9H_9O_2N_3$: C 53.62; H 5.06; N 23.45.

α-(2-Pyridylamino)phenylacetnitril (XI).—Man versetzt 10.6 g Benzaldehyd mit einer Lösung von 10.4 g Natriumbisulfit in 25 ccm Wasser, erhitzt 1

Std und dann versetzt man es mit 9.4 g 2-Aminopyridin. Nach 3 stdg. Erhitzen setzt man dazu 6.5 g Kaliumcyanid in wenigem Wasser zu, rührt 2~3 Std bei Raumtemperatur um und filtriert den gebildeten gelben Niederschlag ab. Gelbe Nadeln vom Schmp. 210~211°C (aus Äthanol). Ausbeute 8.5 g (40%).

Gef.: N 20.15. Ber. für $C_{13}H_{11}N_3$: N 20.08.

4-Phenyl-5-benzylidenaminopyrimidazol (II).—Eine Lösung von 2 g XI und 1 g Benzaldehyd in 10 ccm Äthanol wird 2 Std am Rückfluß erhizt und dann eingeengt. Es hinterbleibt ein gelbes Fett, das aus Ligroin umkristallisiert wird. Gelbe Nadeln vom Schmp. 137°C. Ausbeute nah-quantitativ.

Gef.: C 80.86; H 5.37; N 13.94. Ber. für $C_{20}H_{15}N_3$: C 80.80; H 5.05; N 14.14.

α-(2-Pyridylamino)propionitril (IX).—Man versetzt eine Lösung von 10.5 g Natriumbisulfit in 20 ccm Wasser mit 10 g. von 44 proz. Acetaldehyd, erhitzt 1 Std auf dem Wasserbad und dann fügt man 9.4 g 2-Aminopyridin hinzu. Nach 2 stdg. Erhitzen setzt man 7 g Natliumcyanid, in 10 ccm von heissem Wasser gelöst zu, und erhitzt es unter mechanischem Rühren 2 Std auf dem Wasserbad. Das abgeschiedene Öl kristallisiert beim Abkühlen bis Raumtemperatur. Ausbeute 8 g. Gelbliche Nadeln vom Schmp. 133~135°C (aus Benzol).

Gef.: N 28.33. Ber. für $C_9H_9N_3$: N 28.57.

4-Methyl-5-benzylidenaminopyrimidazol (X).—Eine Lösung von 1 g IX und 1 g Benzaldehyd in 10 ccm Äthanol wird 2 Std am Rückfluß erhitzt und das Gemisch wird wie vorstehend aufgearbeitet, wobei 1.5 g X erhalten wird. Gelbe Schuppen vom Schmp. 52~56°C (aus Ligroin).

Gef.: N 17.59. Ber. für $C_{15}H_{13}H_3$: N 17.86.

Herrn Asaji Kondo für die Ausführung der Mikroanalysen und Dr. Tadashi Sato (Waseda Universität) für die Aufnahme der IR-Spektren danken wir bestens.

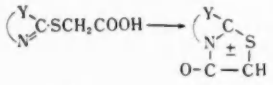
Organisch-Chemisches Laboratrium
Technische Hochschule zu Tokyo
Meguro-ku, Tokyo

Studies on Meso-ionic Compounds. XII[1]*. Reaction between Acetic Anhydride and Azoles having Carboxymethylmercapto-group**

By Mutsuko HASHIMOTO and Masaki OHTA

(Received April 14, 1960)

Duffin et al.[2,3] already reported that when a heterocyclic-compound of the type I was subjected to the action of acetic anhydride, water was eliminated and a ring closure followed to give a meso-ionic compound of the type II.



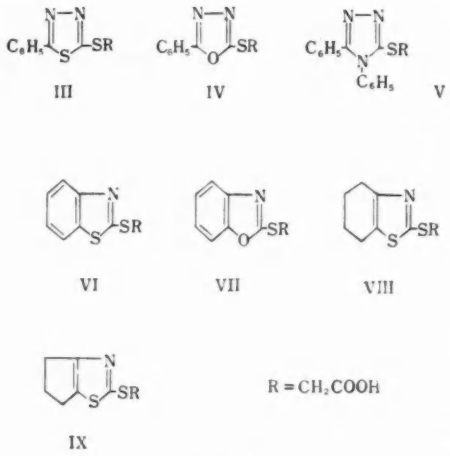
I II

Y=Remainder of heterocyclic nucleus.

Fig. 1

The heterocyclic nuclei used by them were pyridine, quinoline, imidazole and benzimidazole.

In the present paper, this reaction is extended further to several kinds of azoles containing oxygen or sulfur (III–IX), and their behavior to acetic anhydride is investigated in detail.



III IV V

VI VII VIII

IX

R=CH_2COOH

Fig. 2

Action of Acetic Anhydride on the Azoles.—5-Phenyl-1, 3, 4-thiadiazolyl-2-thioglycollic acid (III) is sparingly soluble in acetic anhydride at room temperature, while being heated on a

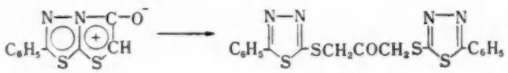
1) Part XI. M. Masaki and M. Ohta, This Bulletin, 33, 1392 (1960).

* Presented at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April 2, 1959.

2) G. F. Duffin and J. D. Kendall, *J. Chem. Soc.*, **1951**, 734.

3) G. F. Duffin and J. D. Kendall, ibid., **1956**, 361.

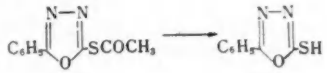
water bath, it dissolves in acetic anhydride and the solution quickly turns from yellow to dark red, and after 5 min. yellow crystals separate, which can be recrystallized unchanged from acetic anhydride. Elemental analysis indicates the compound to be an anhydro-compound of the structure X**, which is also supported by infrared analysis described below. When refluxed gently with 50% aqueous sulfuric acid or pyridine, the anhydro-compound X gives bis-5-phenyl-1, 3, 4-thiadiazolyl-2-thioacetone (XI).



X XI

Fig. 3

When 5-phenyl-1, 3, 4-oxadiazolyl-2-thioglycollic acid (IV) is boiled in acetic anhydride, no intense color develops, but 5-phenyl-1, 3, 4-oxadiazolyl-2-thioacetate (XII) is obtained. The product XII is hydrolyzed to 2-mercapto-5-phenyl-1, 3, 4-oxadiazole (XIII) with 10% aqueous sodium hydroxide.

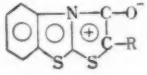


XII XIII

Fig. 4

Under similar conditions, 1, 5-diphenyl-1, 3, 4-triazolyl-2-thioglycollic acid (V) gives no pure reaction product.

When benzothiazolyl-2-thioglycollic acid (VI) is dissolved in acetic anhydride and the solution is warmed, it rapidly becomes dark red, and lustrous red-purple crystals separate. The compound is sparingly soluble in organic solvents and so difficult to burn that its elemental analysis corresponds to $C_{11}H_7O_2NS_2$ for the acetyl derivative of an anhydro-compound (XIVa; R=$COCH_3$) with a difference of 1% or so in the carbon content. However, the same colored crystals are obtained by the action of propionic anhydride instead of acetic anhydride on the acid VI, and consequently the assignment of the structure XIVa for the colored compound would not be correct.

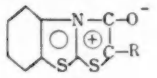


XIV

Fig. 5

On being treated with acetic anhydride, benzoxazolyl-2-thioglycollic acid (VII) gives only a yellow gummy material.

When cyclohexenothiazolyl-2-thioglycollic acid (VIII) is warmed in acetic anhydride, an orange color quickly develops which gradually changes to intense blue-violet, and black-violet crystals separate. The compound is as sparingly soluble in organic solvents and as difficult to burn as that obtained from the acid VI. Elemental analysis of the compound corresponds to $C_{11}H_{11}O_2NS_2$ with a difference of 1% or so in the carbon content. Although the formula $C_{11}H_{11}O_2NS_2$ suggests the structure of the acetyl derivateve of an anhydro-compound derived from the acid VIII (XVa; R=$COCH_3$), this structure should be excluded by the fact that the same compound is also obtained on treating with propionic anhydride.



XV

Fig. 6

The infrared spectra of the compounds $C_{11}H_7O_2NS_2$ and $C_{11}H_{11}O_2NS_2$ are similar to each other and show that there is great resemblance between structures of both compounds, and these structures are under investigation.

Action of Acetic Anhydride and Pyridine or Triethylamine on the Azoles.—When 5-phenyl-1, 3, 4-thiadiazolyl-2-thioglycollic acid (III) is added to a mixture of acetic anhydride and dry pyridine (volume ratio of 1 : 2), a yellow color immediately develops and the color changes to orange as the acid III dissolves. After several minutes yellow crystals separate, which are identical with the anhydro-compound X described above.

Under similar conditions, 5-phenyl-1, 3, 4-oxadiazolyl-2-thioglycollic acid (IV) affords 5-phenyl-1, 3, 4-oxadiazolyl-2-thioacetate (XII) which is obtained from IV by treating with acetic anhydride only, while 1, 5-diphenyl-1, 3, 4-triazolyl-2-thioglycollic acid (V) is recovered unchanged.

When benzothiazolyl-2-thioglycollic acid (VI) is added to acetic anhydride and dry pyridine (volume ratio of 1 : 2), the mixture immediately turns yellow as the acid VI dissolves, and the color finally becomes dark green. After a few minutes blue-green crystals separate, from which yellow needles are obtained by extraction with benzene. Elemental analysis shows

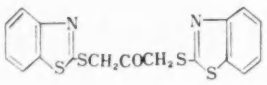
** The formulation adopted is that put forward by Baker and Ollis. W. Baker and W. D. Ollis, *Quart. Rev.*, **11**, 15 (1957); W. Baker, *Proc. Chem. Soc.*, **1959**, 75.

the compound to be an anhydro-compound of the structure (XIVb; R=H), which is also supported by infrared analysis described below.

Besides the anhydro-compound XIVb, the lustrous red-purple crystals are obtained from the benzene-insoluble portion in a considerable yield.

When the acid VI is dissolved in a mixture of acetic anhydride and triethylamine (volume ratio of 1:2), a yellow color develops and yellowish-brown crystals separate, which are recrystallized from benzene to yield the anhydro-compound XIVb.

On refluxing gently with pyridine the anhydro-compound XIVb affords bisbenzothiazolyl-2-thioacetone (XVI), which is identical with a specimen prepared from sym-dichloroacetone and 2-mercaptobenzothiazole. With hot 50% aqueous sulfuric acid the compound XIVb affords the compound XVI and the parent acid VI.



XVI

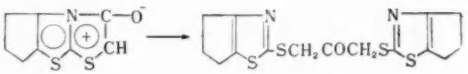
Fig. 7

When benzoxazolyl-2-thioglycollic acid (VII) is treated with acetic anhydride in pyridine or triethylamine, no anhydro-compound can be obtained but the starting material is recovered.

When cyclohexenothiazolyl-2-thioglycollic acid (VIII) is dissolved in a mixture of acetic anhydride and dry pyridine (volume ratio of 1:2), a deep yellow color quickly develops which gradually changes to blue-green, and light blue crystals separate. Extraction of the crystals with benzene gives benzene-soluble light green needles and the benzene-insoluble black-violet crystals. The former compound is also obtained exclusively on treating the acid VIII with acetic anhydride and triethylamine. Elemental analysis of the compound indicates that it is not an anhydro-compound of the structure (XVb; R=H), but a compound of the formula $C_{10}H_9ONS_2$.

With hot 50% aqueous sulfuric acid the compound $C_{10}H_9ONS_2$ is hydrated to the parent acid VIII, and with boiling pyridine it affords a compound of the formula $C_8H_{11}ONS_2$. The structures of both compounds $C_{10}H_9ONS_2$ and $C_8H_{11}ONS_2$ await further investigation.

When cyclopentenothiazolyl-2-thioglycollic acid (IX) is dissolved in a mixture of acetic anhydride and triethylamine (volume ratio of 1:2), deep yellow crystals immediately separate, which are shown to be an anhydro-compound of the structure XVII by elemental and infrared analyses. The compound XVII is hydrated to the parent acid IX with hot 50% aqueous sulfuric acid, and with boiling pyridine it affords monohydrate of biscyclopentenothiazolyl-2-thioacetone (XVIII).



XVII XVIII

Fig. 8

It seems very interesting that the behavior of the acid VIII to acetic anhydride and triethylamine differs greatly from that of the acid IX; nevertheless, the structures of two acids nearly the same. However, the question what factor of the acids can give rise to such a significant difference remains obscure.

The results presented in this paper speak for themselves. Several points deserve further comment, however.

In the first place, it is clear that the azoles free from sulfur in their nuclei; IV, V and VII give no intensely colored compounds like the compounds $C_{11}H_{11}O_2NS_2$ and $C_{11}H_9O_2NS_2$ on treating with acetic anhydride. Duffin et al., on the other hand, did not report that such a colored compound was obtained. Consequently, it is considered that the reaction center in formation of the colored compounds might be at the ring-sulfur of heterocycle.

It is also clear that the azoles containing sulfur in their nuclei; III, VI and IX can be subjected to two different types of reactions to give the colored compound and the anhydro-compound like X, XIVb and XVII, respectively.

The mechanism of formation of the anhydro-compounds is obscure, but in this case the reaction center seems to be at the ring-nitrogen of heterocycle.

Infrared Analyses of the Anhydro-compounds X, XIVb and XVII.—The infrared spectra of the anhydro-compounds, their parent acids and decomposition products were taken.

When the spectra of the anhydro-compounds are compared with those of their parent acids, three remarkable changes can be observed. Firstly, the disappearance of the band at 1720~1708 cm^{-1} due to the C=O vibration of carboxylic group and the appearance of a band at 1645 cm^{-1}, which is probably due to the amide I band of tertiary amide. Secondly, the appearance of a new strong band near 1600 cm^{-1}, which disappears again in the spectrum of the decomposition product. Consequently, this band seems to be produced by formation of a meso-ionic ring, but the assignment of the band is still unknown. Lastly, the red

shift of 35 cm^{-1} or so of the band at 1180± 10 cm^{-1}.

The three remarkable changes mentioned above can be also observed in the spectra of the anhydro-compound derived from (2-pyridylthio)acetic acid, whose structure has been confirmed synthetically.[2]

Experimental

5-Phenyl-1, 3, 4-thiadiazolyl-2-thioglycollic Acid (III).—This acid was prepared by Sato's method[4].

Anhydro-compound X from III. — (a) A solution of the acid III (5.0 g.) in acetic anhydride (100 ml.) was heated on a boiling water bath for 5 min., quickly turning from yellow to red. Yellow crystals which separated were filtered off and recrystallized from acetic anhydride to give the anhydro-compound as small yellow needles (1.9 g.), m. p. 231°C (decomp.).

Found: C, 51.54; H, 2.80; N, 11.71. Calcd. for $C_{10}H_6ON_2S_2$: C, 51.29; H, 2.58; N, 11.96%.

(b) III (1.0 g.) was dissolved with stirring at room temperature in a mixture of acetic anhydride (3 ml.) and dry pyridine (6 ml.). A yellow color immediately developed and the color changed to orange. After several minutes yellow crystals separated, which were filtered off after 0.5 hr., washed with water, and dried to give deep yellow crystals (0.6 g.), m. p. 229~230°C (decomp.). Recrystallization from acetic anhydride gave small yellow needles, m. p. 231°C (decomp.).

Found: N, 11.70. Calcd. for $C_{10}H_6ON_2S_2$: N, 11.96%.

Action of Aqueous Sulfuric Acid on the Anhydro-compound X.—X (1.0 g.) was refluxed gently with 50% aqueous sulfuric acid (10 ml.) for 10 min. The cooled solution was diluted with water (50 ml.) to give a crystalline precipitate which was filtered off and recrystallized from ethanol, affording small colorless needles of bis-5-phenyl-1, 3, 4-thiadiazolyl-2-thioacetone (XI) (0.69 g.), m. p. 148°C.

Found: C, 51.36; H, 3.42; N, 12.75; S, 29.06; mol. wt. (Rast), 455. Calcd. for $C_{19}H_{14}ON_4S_4$: C, 51.58; H, 3.17; N, 12.67; S, 28.96%; mol. wt., 442.

Action of Pyridine on X.—X (0.3 g.) was refluxed gently with pyridine (10 ml.) for 5 min. After cooling, the solution was diluted with water (50 ml.) to give a crystalline precipitate (0.24 g.), m. p. 146 ~147°C. Recrystallization from ethanol yielded small colorless needles, m. p. 148°C, undepressed by admixture with XI.

5-Phenyl-1, 3, 4-oxadiazolyl-2-thioglycollic Acid (IV).—A solution of chloroacetic acid (2.0 g.) and sodium carbonate (1.1 g.) in water (20 ml.) was added to a solution of crude 2-mercapto-5-phenyl-1, 3, 4-oxadiazole (3.0 g.) and potassium hydroxide (1.0 g.) in water (30 ml.). The solution was kept to stand at room temperature overnight, neutralized with dilute hydrochloric acid. The resulting precipitate was filtered off, dissolved in aqueous sodium bicarbonate to remove insoluble impurities and neutralized with dilute hydrochloric acid. After filtration and drying 5-phenyl-1, 3, 4-oxadiazolyl-2-thioglycollic acid was obtained (5.0 g.), m. p. 157~162°C. Recrystallization from hot water gave white needles, m. p. 168~169°C.

Found: N, 12.15. Calcd. for $C_{10}H_8O_3N_2S$: N, 12.86%.

Action of Acetic Anhydride on IV. — The acid IV (1.0 g.) and acetic anhydride (10 ml.) were boiled under reflux for 0.5 hr. The anhydride was evaporated under reduced pressure and the residue was recrystallized from ethanol to give 5-phenyl-1, 3, 4-oxadiazolyl-2-thioacetate (XII) as colorless needles (0.22 g.), m. p. 152.5~153°C.

Found: C, 54.33; H, 3.63; N, 12.74. Calcd. for $C_{10}H_8O_2N_2S$: C, 54.54; H, 3.64; N, 12.73%.

XII was dissolved in 10% aqueous sodium hydroxide and then neutralized with 10% aqueous sulfuric acid to give colorless needles, m. p. 217°C, undepressed by admixture with authentic 2-mercapto-5-phenyl-1, 3, 4-oxadiazole.

1, 5-Diphenyl-1, 3, 4-triazolyl-2-thioglycollic Acid (V).—This acid was prepared by Ueda's method[5].

Action of Acetic Anhydride on V.—The acid V (0.5 g.) and acetic anhydride (10 ml.) were boiled under reflux for 0.5 hr., affording a yellow solution. On addition of water (100 ml.) the solution yielded a pale brown gummy material from which no pure compound could be isolated.

Benzothiazolyl-2-thioglycollic Acid (VI).—This acid was prepared by Ohta's method[6].

Action of Acetic Anhydride on VI.—The acid VI (1.0 g.) was added to acetic anhydride (20 ml.) and warmed on a water bath. The solution rapidly became dark red and at the same time crystals separated, which were filtered off and washed with hot ethanol, giving lustrous red-purple crystals (0.57 g.), m. p. 297°C.

The anhydride filtrate was diluted with water (100 ml.) and washed with hot ethanol to give lustrous red-purple crystals (0.35 g.), m. p. 297°C. Total yield, 0.92 g.

Found: C, 51.80; H, 3.00; N, 5.85. Calcd. for $C_{11}H_7O_2NS_2$: C, 53.01; H, 2.81; N, 5.62%.

The above experiment was repeated but with propionic anhydride instead of acetic anhydride, the same product being obtained.

Benzoxazolyl-2-thioglycollic Acid (VII).—A solution of chloroacetic acid (1.9 g.) and sodium carbonate (1.06 g.) in water (20 ml.) was added to a solution of 2-mercaptobenzoxazole (3.0 g.) and sodium hydroxide (0.8 g.) in water (20 ml.). The solution was warmed on a water bath for 0.5 hr. and kept standing at room temperature overnight. After neutralization with dilute hydrochloric acid, the resulting precipitate was filtered off, washed with water and recrystallized from dilute ethanol to give colorless plates of VII (3.85 g.), m. p. 160~161°C.

Found: N, 6.27. Calcd. for $C_9H_7O_3NS \cdot H_2O$; N, 6.17%.

Action of Acetic Anhydride on VII.—The acid VII (1.0 g.) was refluxed gently with acetic anhydride (10 ml.) for 0.5 hr., affording a deep yellow

4) T. Sato and M. Ohta, *J. Pharm. Soc. Japan*, **77**, 771 (1957).

5) H. Ueda, unpublished work.

6) H. Ohta and M. Ohta, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 700 (1957).

solution. The anhydride was evaporated under reduced pressure, the residue of violet gum extracted with ether and the extract evaporated to dryness to give yellowish gummy material which could not be purified.

Cyclohexenothiazolyl-2-thioglycollic Acid (VIII).—This acid was prepared by the same process as used for benzothiazolyl-2-thioglycollic acid (VI)[6]. Colorless lancets, m. p. 124~125°C. Yield, 80.4%.

Action of Acetic Anhydride on VIII.—The acid VIII (1.0 g.) was added to acetic anhydride (2 ml.) and warmed on a water bath. An orange color quickly developed which gradually changed to intense blue-violet, and black-violet crystals separated. The crystals were filtered off and washed with hot ethanol to give black-violet crystals (0.7 g.), m. p. 254.5~255°C (decomp.).

The anhydride filtrate was diluted with water (200 ml.), and the resulting precipitate was filtered off and washed with hot ethanol to give black-violet crystals (0.02 g.), m. p. 254.5~255°C (decomp.). Total yield, 0.76 g.

Found: C, 50.84; H, 4.35; N, 5.72. Calcd. for $C_{11}H_{11}O_2NS_2$: C, 52.17; H, 4.35; N, 5.53%.

The above experiment was repeated but with propionic anhydride instead of acetic anhydride, the same product being obtained.

Action of Acetic Anhydride and Pyridine on IV.—The acid IV (1.0 g.) was refluxed in a mixture of acetic anhydride (5 ml.) and dry pyridine (5 ml.) for 0.5 hr. and the solvent was removed in vacuo to give a black oil, which was solidified by addition of a small amount of ethanol. Recrystallization from ethanol gave XII as colorless needles (0.12 g.), m. p. 149~150°C, undepressed by admixture with authentic sample.

Action of Acetic Anhydride and Pyridine on V.—The acid V (0.5 g.) was refluxed in a mixture of acetic anhydride (3 ml.) and dry pyridine (6 ml.) for 5 min., the solvent removed in vacuo and the residue recrystallized from ethanol to give colorless needles, m. p. 238°C, undepressed by admixture with the acid V.

Found: N, 13.65. Calcd. for $C_{16}H_{13}O_2N_3S$: N, 13.50%.

Anhydro-compound XIVb from VI.—(a) The acid VI (1.0 g.) was dissolved with stirring at room temperature in a mixture of acetic anhydride (3 ml.) and dry pyridine (6 ml.). The solution immediately turned yellow and the color finally became dark green. After a few minutes crystals separated, which were filtered off, washed thoroughly with water, dried and then extracted with hot benzene. The extract was evaporated to dryness giving yellow crystals (0.3 g.), m. p. 209~212°C (decomp.). Recrystallization from benzene yielded the anhydro-compound as bright yellow leaflets, m. p. 215~216°C (decomp.).

Found: C, 51.94; H, 2.58; N, 6.89. Calcd. for $C_9H_5ONS_2$: C, 52.18; H, 2.43; N, 6.76%.

From the benzene-insoluble portion, the lustrous red-purple crystals were obtained (0.33 g.).

(b) VI (1.0 g.) was dissolved with stirring at room temperature in a mixture of acetic anhydride (3 ml.) and triethylamine (6 ml.), a yellow color quickly developing. After a few minutes yellowish brown crystals separated, which were filtered off, washed thoroughly with water, dried and extracted with hot benzene. The extract was evaporated to dryness to give yellow crystals (0.47 g.), m. p. 210~212°C (decomp.). Recrystallization from benzene yielded the anhydro-compound as bright yellow leaflets, m. p. 216~216.5°C (decomp.).

Found: N, 6.55. Calcd. for $C_9H_5ONS_2$: N, 6.76%.

Action of Pyridine on the Anhydro-compound XIVb.—XIVb (0.3 g.) was refluxed gently with pyridine (10 ml.) for 5 min. After cooling, the solution was diluted which water (50 ml.) to give a crystalline precipitate with was filtered off and recrystallized from ethanol, affording bisbenzothiazolyl-2-thioacetone (XVI) as colorless needles (0.18 g.), m. p. 127°C, undepressed by admixture with authentic sample.

Found: N, 7.36. Calcd. for $C_{17}H_{12}ON_2S_4$: N, 7.21%.

Bisbenzothiazolyl-2-thioacetone.—To a solution of 2-mercaptobenzothiazole (5.5 g.) in absolute ethanol (50 ml.) containing metallic sodium (0.8 g.) was added *sym*-dichloroacetone (2.0 g.). After 5 min. crystals separated at a time. The crystals were filtered off, washed with water and recrystallized twice from ethanol to give colorless needles (8.0 g.), m. p. 127°C.

Found: C, 52.83; H, 3.37; N, 7.18. Calcd. for $C_{17}H_{12}ON_2S_4$: C, 52.56; H, 3.09; N, 7.21%.

Action of Aqueous Sulfuric Acid on XIVb.—XIVb (0.3 g.) was refluxed gently with 50% aqueous sulfuric acid (10 ml.) for 10 min. and the cooled solution was diluted with water (50 ml.) to give a crystalline precipitate which was filtered off and recrystallized from ethanol, affording colorless needles (0.05 g.), m. p. 124°C, undepressed by admixture with authentic sample of XVI. Addition of water to the mother-liquor precipitated pale yellow prisms (0.06 g.), m. p. 157~158°C, undepressed by admixture with the acid VI.

Action of Acetic Anhydride and Pyridine on VII.—The acid VII (1.0 g.), acetic anhydride (1 ml.) and dry pyridine (3 ml.) were heated on a boiling water bath for 0.5 hr. and after cooling, the solution was concentrated under reduced pressure to give colorless leaflets (0.9 g.), m. p. 160~162°C, undepressed by admixture with the acid VII.

Action of Acetic Anhydride and Triethylamine on VII.—The acid VII (1.0 g.) was dissolved in a mixture of acetic anhydride (1 ml.) and triethylamine (3 ml.) and the solution kept to stand at room temperature for 3 hr. The solution was concentrated under reduced pressure to give an orange oily material, which rapidly solidified by addition of water. Colorless leaflets (0.91 g.), m. p. 163°C, undepressed by admixture with the acid VII.

Action of Acetic Anhydride and Pyridine on VIII.—The acid VIII (1.0 g.) was dissolved with stirring at room temperature in a mixture of acetic anhydride (3 ml.) and dry pyridine (6 ml.). A deep yellow color quickly developed which gradually changed to blue-green and light blue crystals separated. After 0.5 hr., the crystals were filtered off, washed thoroughly with water, dried and then

extracted with hot benzene and the extract was evaporated to dryness to give light green needles (0.52 g.), m. p. 198~199°C (decomp.). Recrystallization from benzene gave m. p. 198~199°C (decomp.).

Found: C, 53.51; H, 4.60; N, 6.08. Calcd. for $C_{10}H_9ONS_2$: C, 53.81; H, 4.06; N, 6.28%.

From the benzene-insoluble portion, the black-violet crystals were obtained (0.17 g.).

Action of Acetic Anhydride and Triethylamine on VIII.—The acid VIII (1.0 g.) was dissolved with stirring at room temperature in a mixture of acetic anhydride (3 ml.) and triethylamine (6 ml.). Light brown crystals rapidly separated, which were filtered off, washed thoroughly with water, dried and extracted with hot benzene. The extract was evaporated to dryness to give light yellow crystals (0.68 g.), m. p. 197~199°C (decomp.). Recrystallization from benzene yielded light yellow needles, m. p. 198°C (decomp.).

Found: N, 6.26. Calcd. for $C_{10}H_9ONS_2$: N, 6.28%.

Action of Aqueous Sulfuric Acid on the Compound $C_{10}H_9ONS_2$.—The compound (0.5 g.) was refluxed gently with 50% aqueous sulfuric acid (12 ml.) for 0.5 hr. The cooled solution was diluted with water (50 ml.) and extracted with ether. The ether extract was evaporated and the residue recrystallized from ethanol to give colorless prisms, m. p. 125~126°C, undepressed with the acid VIII.

Found: N, 5.94. Calcd. for $C_9H_{11}O_2NS_2$: N, 6.11%.

Action of Pyridine on the Compound $C_{10}H_9ONS_2$.—The compound (1.0 g.) was refluxed gently with pyridine (20 ml.) for 20 min. After cooling, the solution was diluted with water (150 ml.) and colorless needles which separated were filtered off and dried. M. p. 94.5°C, 1.0 g. Recrystallization from dilute pyridine gave colorless silky needles, m p. 98.5~99.5°C.

Found: C, 47.60; H, 5.35; N, 6.86; S, 31.1. Calcd. for $C_8H_{11}ONS_2$: C, 47.76; H, 5.47; N, 6.97; S, 31.84%.

Cyclopentenothiazolyl-2-thioglycollic Acid (IX).—This acid was prepared by the same process as used for benzothiazolyl-2-thioglycollic acid (VI)[6]. Colorless needles, m. p. 126°C, yield, 45.6%.

Anhydro-compound XVII from IX.—The acid IX (1.0 g.) was dissolved with stirring at room temperature in a mixture of acetic anhydride (3 ml.) and triethylamine (6 ml.). After one minute crystals separated, which were filtered off, washed thoroughly with water and dried. M. p. 198~201°C, 0.67 g. Recrystallization from benzene gave the anhydro-compound as deep yellow crystals, m. p. 213.5~214°C (decomp.).

Found: C, 48.65; H, 3.97; N, 7.20. Calcd. for $C_8H_7ONS_2$: C, 48.74; H, 3.58; N, 7.11%.

Action of Aqueous Sulfuric Acid on the Anhydro-compound XVII.—XVII (0.5 g.) was dissolved in 50% aqueous sulfurid acid (12 ml.) and the resultant yellow solution refluxed gently for 10 min., the yellow color disappearing. The solution was diluted with water (150 ml.), neutralized with sodium carbonate, extracted with ether and the extract evaporated to give colorless needles (0.38 g.), m. p. 117°C. Recrystallization from dilute ethanol gave colorless needles, m. p. 124~126°C, undepressed by admixture with the acid IX.

Found: N, 6.41. Calcd. for $C_9H_9O_2NS_2$: N, 6.51%.

Action of Pyridine on XVII.—XVII (0.3 g.) was refluxed gently with pyridine (10 ml.) for 5 min. The solution was diluted with water (50 ml.) and a crystalline precipitate filtered off, washed with water and dried. M. p. 81.5°C, 0.27 g. Recrystallization from dilute ethanol afforded colorless silky needles, m. p. 81~82°C.

Found: C, 46.39; H, 4.83; N, 7.53. Calcd. for $C_{15}H_{16}ON_2S_4 \cdot H_2O$: C, 46.63; H, 4.66; N, 7.25%.

The authors are indebted to Mr. Asaji Kondo for performing the microanalyses and to Dr. Tadashi Sato for assistance in the infrared determinations.

Laboratory of Organic Chemistry
Tokyo Institute of Technology
Meguro-ku, Tokyo

Polyaddition Reaction of Diphenylsilane to Difunctional Unsaturated Compounds. II

By Kuniharu KOJIMA

(Received March 22, 1960)

Several literatures have been published on the addition reaction of silicon hydrides to a number of olefines using peroxide, ultraviolet light, γ-rays or platinum catalysts.

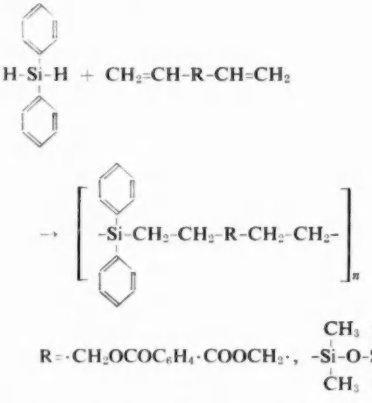
In 1947, L. H Sommer reported that *n*-octyltrichlorosilane was prepared by the addition reaction of 1-octene with trichlorosilane in the presence of a small amount of diacetyl peroxide catalysts at 50~63°C[1,2]. This addition reaction was also carried out using γ-rays from a 30 kilocurie Co^{60} source at room temperature in an almost quantitative yield[3].

The addition reaction of trichlorosilane to styrene was first carried out by C. A. Burkhard in the presence of peroxide catalysts, resulting in the formation of only non-volatile telomeric products[4]. W. S. Wagner and coworkers succeeded in the preparation of β-phenylethyltrichlorosilane by the above mentioned addition reaction using platinized charcoal as the catalyst at 200°C[5]. S. Nozakura reported the formation of α- and β-trichlorosilylethylbenzene by the same reaction using tetrapyridine nickel chloride as the catalyst at 160°C[6]. The platinum catalyzed addition reaction of methyldichlorosilane with methyl methacrylate was carried out by L. H. Sommer and coworkers in the preparation of α-methyl-β-methyldichlorosilyl propionate[7].

The addition reaction of methyldichlorosilane with vinyl acetate was studied by J. L. Speier and coworkers in the preparation of 2-methyldichlorosilylethyl acetate[8]. L. Goodman reported similar reactions of various silanes (phenylsilane, methyldiethoxysilane, trichlorosilane or methyldichlorosilane to allyl acetate[9]. J. W. Curry and coworkers have recently described the polymerization of certain silanes having an unsaturated organic group and a hydrogen on the same silicon atom[10,11].

1) L. H. Sommer et al., *J. Am. Chem. Soc.*, **69**, 188 (1947).
2) L. H. Sommer et al., ibid., **70**, 484 (1948).
3) L. C. Anderson et al., ibid., **80**, 1737 (1958).
4) C. A. Burkhard et al., ibid., **69**, 2687 (1947).
5) W. S. Wagner et al., *Ind. Eng. Chem.*, **45**, 367 (1953).
6) S. Nozakura., This Bulletin, **29**, 784 (1956).
7) L. H. Sommer et al., *J. Am. Chem. Soc.*, **79**, 2764 (1957).
8) J. L. Speier et al., ibid., **79**, 974 (1957).
9) L. Goodman et al., ibid., **79**, 3073 (1957).
10) J. W. Curry, ibid., **78**, 1689 (1956).
11) J. W. Curry et al., *J. Org. Chem.*, **23**, 1219 (1958).

In the previous paper, we have reported the result of the polyaddition reaction of diphenylsilane with diallyl phthalate or methyldisiloxane in the presence of a small amount of platinum black[12].



$$R = -CH_2OCOC_6H_4\cdot COOCH_2-,\quad -\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-$$

By these reactions carried out in sealed glass tubes, new polymers containing silicon were obtained in good yield. As a continuation of the experiment, the present paper deals with a new synthetic method of polymers which can be generally applied to the polyaddition reaction of diphenylsilane with various difunctional unsaturated compound (diallyl adipate, divinyl adipate, tetramethylene dimethacrylate, divinylbenzene and hexadiene).

Our first work was to examine the polyaddition reaction of diphenylsilane with diallyl phthalate using platinum black as the catalyst. As the extension of this work, the effect of various catalysts (i.e. platinum black, chloroplatinic acid, benzoyl peroxide, *tert*-butyl hydroperoxide, and azobisisobyturonitrile) has been studied. The results are shown in Table I.

Platinum catalysts were more effective than other catalysts. The effect of the irradiation of γ-ray or ultraviolet light in this reaction was hardly recognized at room temperature.

Similarly, by the polyaddition reaction of diphenylsilane with diallyl adipate was also prepared a linear polyaddition product in a

12) K. Kojima, This Bulletin, **31**, 663 (1958).

TABLE I. POLYADDITION OF DIPHENYLSILANE WITH DIALLYL PHTHALATE

Catalyst (mol.)	React. time (hr.)	Temp. (°C)	Yield (%)	Mol. wt.
Pt-black, $2 \cdot 10^{-4}$	50	110~20	76	2390
Chloroplatinic acid, $2 \cdot 10^{-6}$	〃	〃	73	2060
Benzoyl peroxide, $2 \cdot 10^{-4}$	〃	〃	60	955
tert-Butyl hydroperoxide, $2 \cdot 10^{-4}$	〃	〃	67	765
Azobisisobutyronitrile, $2 \cdot 10^{-4}$	〃	〃	69	775

In these experiments, 0.02 mol. of diphenylsilane and 0.02 mol. of diallyl phthalate were used.

76% yield. The molecular weight of this polyadduct was 1400.

In the polyaddition reaction of diphenylsilane with divinyl adipate using platinum black as catalyst, however, the linear polyaddition product was obtained in 34% yield and the other polyadduct was a highly branched (or a cross-linked) polymer. The molecular weight of the linear polymer was 1660. The combination ratio of divinyl adipate and diphenylsilane of the branched polymer was 4 : 1.

The reaction of diphenylsilane with tetramethylene dimethacrylate did not produce a linear high polymer, but gave a low molecular weight adduct (mol. wt. 460) in 37% yield and a branched polymer (combination ratio, tetramethylene dimethacrylate 2 moles : diphenylsilane 1 mole).

When diphenylsilane and divinylbenzene were heated at 120°C in the presence of Pt-black, the highly branched polymer and low molecular weight adducts were obtained. The molecular weight of this low-adduct was 440. The combination ratio of branched polymer was diphenylsilane 1 mol. : divinylbenzene 18 mol.

In the addition reaction of diphenylsilane with hexadiene using platinum black catalyst, the low molecular weight adduct (mol. wt. 685) was only obtained in a 43% yield.

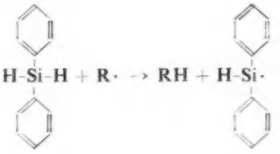
The mechanism of the addition reaction of silicon hydride to olefinic compounds catalyzed by platinum is not clear yet. But it has been asserted, that the addition reaction of silicon hydride to alkene using peroxide catalyst is a free radical chain reaction[1]. The proposed mechanism for the reaction is

$$R\cdot + HSi\equiv \rightarrow RH + \equiv Si\cdot$$

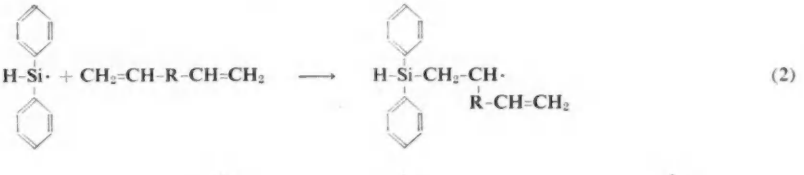
$$RCH{=}CH_2 + \equiv Si\cdot \rightarrow R\dot{C}H{-}CH_2Si\equiv$$

$$R\dot{C}HCH_2Si\equiv + HSi\equiv \rightarrow RCH_2CH_2Si\equiv + \equiv Si\cdot$$

In this paper, the reaction of diphenylsilane with difunctional unsaturated compound to form the linear high molecular weight polymer was predominant.



(1)



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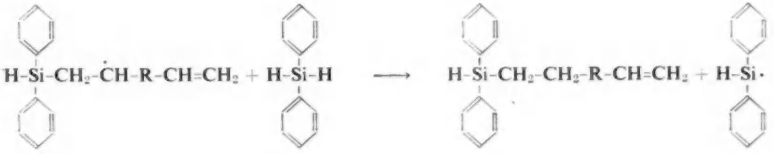

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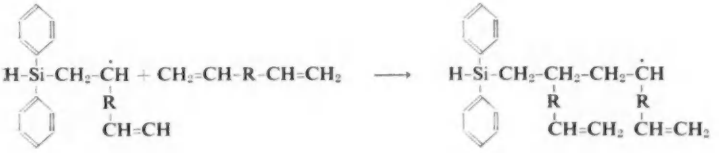


(4)

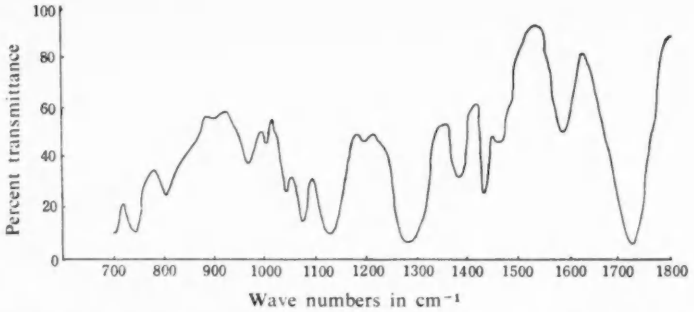


Fig. 1. Infrared spectrum of adduct of diphenylsilane with diallyl phthalate.

But in some cases, it was found that the second reaction shown in Eq. 4 also took place.

This reaction is responsible for the formation of branched polymer and a strong competitor for the normal addition reaction 3. In case of diallyl phthalate, diallyl adipate and hexadiene, only the reaction 3 can proceed. Theerfore it gave linear products only. But, in the case of divinyl adipate, tetramethylene dimethacrylate and divinylbenzene, branched polymers were obtained together with linear polymers.

The addition reaction of silicon hydrides to some unsaturated compounds has been shown to yield two isomers by other investigators[9,13,14]. The addition compound of trichlorosilane to acrylonitrile could be either $NCCH_2CH_2SiCl_3$ (α-adduct) or $NCCH(CH_3)SiCl_3$ (β-adduct).

But, in the case of platinum catalyzed reaction, the addition reactions of silicon hydrides to vinyl acetate and to methyl methacrylate have been shown to yield β-adducts, and the addition to allyl acetate has been shown to yield γ-adducts.

By analogy, the addition compounds of diphenylsilane with each of divinyl adipate, and tetramethylene dimethacylate are presumed to be mainly β-adducts, and the adduct of diallyl phthalate are γ-adduct. But, it was shown, that the infrared absorption spectra of the addition compounds obtained in this work were identical in all important respects with that of the mixture of them.

In the isolation of the polymer, it was found, thats ome volatile by-products are also obtained from the reaction mixture. In the case of tetramethylene dimethacrylate, the volatile product was obtained in considerable quantities, and the yielded gas was identified as propylene and propane by gas-chromatography. But the mechanism of the production of propylene and propane is indistinct.

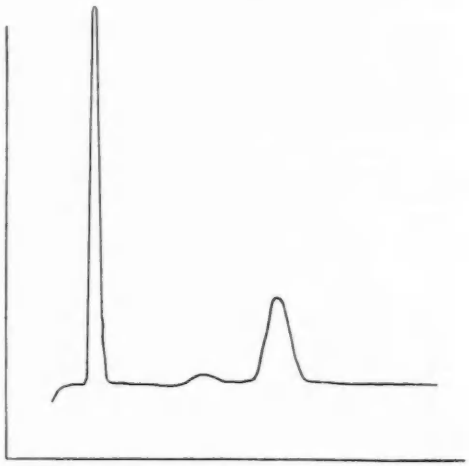


Fig. 2. Gas-chromatograph of the reaction by-products of diphenylsilane with tetramethylene dimethacrylate. Carrier gas, hydrogen; column dimethyl formamid-active charcoal.

Experimental

Materials.—Diallyl adipate[15] and divinyl adipate[16] were prepared by the published methods. Tetramethylene dimethacrylate was prepared by the ester interchange reaction of methyl methacrylate with 1,4-butanediol in the presence of sulfuric acid and hydroquinone[17]. Diallyl phthalate and divinylbenzene were commercial products. Hexadiene was prepared by the reaction of allyl bromide with metallic magnesium in ether[18]. Diphenylsilane was prepared from diphenyldichlorosilane by lithium

13) S. Nozakura et al., ibid., **29**, 322 (1956).
14) S. Nozakura et al., ibid., **29**, 326 (1956).
15) K. Kojima et al., *Reports of the Research Institute of Dental Materials, Japan.*, 8, 136, (1957).
16) K. Kojima et al., ibid., **9**, 38 (1958).
17) K. Kojima et al., ibid., **8**, 144 (1957).
18) L. Vanino, "Handbuch der Präparativen Chemie". Bd. 2, 7 (1937).

aluminum hydride by ordinary method[19]. Diphenyldichlorosilane was supplied by Shin-etu Chem. Co. and redistilled before being used.

Polyaddition of Diphenylsilane with Diallyl Phthalate.—*Method 1—Pt Black Initiation.*—Diallyl phthalate (4.92 g., 0.02 mol.), diphenylsilane (3.68 g., 0.02 mol.) and platinum black (0.03 g.) as catalyst were placed in a glass tube and the tube was sealed in nitrogen stream, and then heated at 110~120°C in an air oven for 50 hr. The reaction product was dissolved in 100 ml. benzene and reprecipitated by 200 ml. methanol. The precipitated material was separated and dried in a vacuum desiccator at 50°C for 7 days. Yield, 76%.

Found: Si, 5.34. Calcd. for $C_{20}H_{26}O_4Si$: Si, 5.83% mol. wt., 2390.

Method 2—Chloroplatinic Acid Initiation.—Under similar condition as described for Pt black initiation, chloroplatinic acid ($2 \cdot 10^{-5}$ mol.) in methanol solution, diphenylsilane (3.65 g.) and dially phthalate (4.92 g.) were heated and the product was reprecipitated. The average molecular weight of this polymer was found to be 2060. Yield 73%.

Method 3—Benzoyl Peroxide Initiation.—The mixture of diphenylsilane (3.68 g.), diallyl phthalate (4.92 g.) and benzoyl peroxide (0.005 g.) were heated in an air oven for 50 hr. at 110~20°C. The reaction gave a linear polymer of mol. wt. 954. Yield 60%.

Method 4—tert-Butyl Hydroperoxide Initiation.—Under similar condition as described above, 0.002 g. of *tert*-butyl hydroperoxide was used as the catalyst. The reaction gave a linear polymer of mol. wt. 765. Yield 67%.

Method 5—Azobisisobutyronitrile Initiation.—Under similar condition as employed in the preceding experiment, diphenylsilane (3.68 g.), diallyl phthalate (4.92 g.), and azobisisobutyronitril (0.003 g.) were traced to produce 5.81 g. of the linear polymer with 69% of theoretical yield. mol. wt. 774.

Method 6—^{60}*Co Initiation.*—Diphenylsilane (3.68 g.) and diallyl phthalate (4.92 g.) were charged in a glass tube. The tube was sealed in dry nitrogen atmosphere, and then exposed to ^{60}Co irradiation at room temperature for 150 hr. at a rate of $2.1 \cdot 10^{-5}$ r.e.p./hr. The molecular weight of this product was 600. Yield 9.8%.

Method 7—Ultraviolet Light Initiation.—The same mixture employed in the preceding experiment was exposed to ultraviolet light irradiation at room temperature for 150 hr. at 10170 c. d. by merucric lamp but the unreacted diphenylsilane and diallyl phthalate were recovered.

Polyaddition of Diphenylsilane with Diallyl Adipate.—A mixture of diphenylsilane (3.68 g.) and diallyl adipate (4.52 g., 0.02 mole) with 0.03 g. platinum black were heated for 50 hrs. at 120°C in a sealed glass tube. The product was dissolved in benzene and reprecipitated by methanol. The average molecular weight of this polymer was found to be 1400. Yield 68%.

Found: Si, 6.69. Calcd for $C_{24}H_{28}OSi$: Si, 6.84%.

Polyaddition of Diphenylsilane with Divinyl Adipate.—Divinyl adipate (3.96 g., 0.02 mole), diphenylsilane (3.68 g., 0.02 mole) and 0.03 g. platinum black as the catalyst were heated at 120°C for 50 hr. in a sealed glass tube. The product was dissolved in benzene and reprecipitated in methanol. The molecular weight of benzene-soluble polymer was 1660.

Found: Si, 7.12. Calcd. for $C_{22}H_{24}O_4Si$: Si, 7.38%. Yield 39%.

The benzene-insoluble polymer was found to be an adduct of diphenylsilane and divinyl adipate at the mole ratio of 1:4.

Found: Si, 3.32. Calcd. for 1:4 adduct: Si, 3.59%.

Polyaddition of Diphenylsilane with Tetramethylene Dimethacrylate.—Tetramethylene dimethacrylate (4.52 g., 0.02 mol.), diphenylsilane (3.68 g., 0.02 mol.) and 0.03 g. platinum black were heated for 50 hr. at 120°C in a sealed glass tube. The product was dissolved in benzene and reprecipitated by methanol. The low molecular weight addition product (benzene-soluble part) was obtained in a 37% yield. The average molecular weight of this polymer was found to be 460. A branched (or cross-linked) polymer was also formed and it has been cleared by Si analysis, that it was the addition product of diphenylsilane and tetramethylene dimethacrylate at the mole ratio of 1:2.

Found: Si, 4.18, Calcd. for 1:2 adduct: Si, 4.18%.

Polyaddition of Diphenylsilane with Divinylbenzene.—Divinylbenzene (2.60 g., 0.02 mol.), diphenylsilane (3.68 g., 0.02 mol.) and platinum black (0.03 g.) were charged in a glass tube. The tube was sealed under the atmosphere of nitrogen and heated in an air oven for 50 hr. at 125~130°C. The product was dissolved in benzene. The average molecular weight of the solubie product was 440. Yield 65%. The insoluble product was an addition product of diphenylsilane 1 mol. and divinylbenzene 18 mol.

Found: Si, 1.11. Calcd. for 1:18 adduct: Si, 1.10%.

Polyaddition of Diphenylsilane with Hexadiene. Hexadiene (1.64 g., 0.02 mol.), diphenylsilane (3.68 g. 0.02 mol.) and platinum black (0.03 g.) were charged in a glass tube, and the tube was sealed under the nitrogen atmosphere and heated in an air oven for 50 hr. at 110~120°C. Only the low molecular weight product (mol. wt. 685) was obtained in a 43% yield.

Found: Si, 9.87. Calcd for $C_{15}H_{22}Si$: Si, 10.78%.

The author is much indebted to Prof. Yoshio Iwakura for his many useful suggestions and to Mr. Niro Tarumi for his help in the experiments. Appreciation is also due to Shin-etu Chem. Co. for their kindness in supplying the diphenyldichlorosilane.

Tokyo Medical and Dental University
Yushima, Bunkyo-ku, Tokyo

19) R. A. Benkeser et al., *J. Am. Chem. Soc.*, **74**, 648 (1952).

Studies on D-Glucosamine Derivatives. V. Some Derivatives of N-Phenyl-D- and L-glucosaminonitrile

By Juji YOSHIMURA

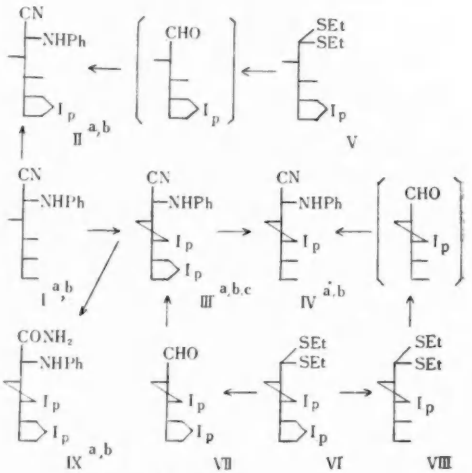
(Received April 22, 1960)

In the preceding paper of this series[1], syntheses of isopropylidene and some other derivatives of D-glucosamine diethylmercaptals were described. In the present paper, the corresponding derivatives of *N*-phenyl-D- and L-glucosaminonitrile were synthesized, and the structure of isopropylidene derivatives were unambiguously confirmed by different derivations.

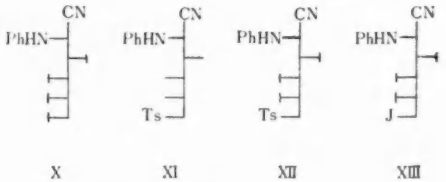
Warming of *N*-phenyl-D- (I^a) or L-glucosaminonitril (I^b), prepared from anhydrous hydrogen cyanide, aniline and D- or L-arabinose by Kuhn's method[2], with anhydrous cupric sulfate in acetone afford the corresponding 5,6-*O*-isopropylidene derivatives (II^a or II^b) respectively, whilst these are converted into the corresponding 3,4 ; 5,6-di-*O*-isopropylidene derivatives (III^a or III^b) by treating with acetone in the presence of concentrated sulfuric acid. III^a and III^b are partially hydrolyzed to the corresponding 3,4-*O*-isopropylidene derivatives (IV^a and IV^b) under an acidic condition.

All these derivations of isopropylidene derivatives are very similar to that of D-glucosamine diethylmercaptals described in Part IV. To determine the position of isopropylidene groups, these were synthesized from isopropylidene *aldehydo*-arabinose, aniline and anhydrous hydrogen cyanide in ethanol. Thus, 2,3;4,5-di-*O*-isopropylidene-*aldehyde*-D-arabinose (VII)[3] was converted in good yield into a mixture of III^a and its epimer ; 3,4 ; 5,6-di-*O*-isopropylidene-*N*-phenyl-D-mannosaminonitrile (III^c). Meanwhile, the unpurified 5,6- and 2,3-*O*-isopropylidene-D-arabinose obtained from the corresponding diethylmercaptal (V)[3] and (VIII) which is the partial hydrolyzed product of 2,3 ; 4,5-di-*O*-isopropylidene-D-arabinose diethylmercaptal (VI)[3] were converted into II^a and IV^a in poor yield.

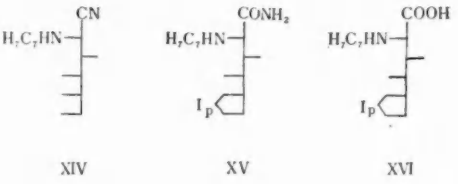
Aldonic acidamides known as an intermediate of Weerman's degradation for shortening the carbon chain of sugars are generally synthesized from aldonic acids or lactones and alcoholic[4] or liquid[5] ammonia. Partial



—·····Hydroxyl group
I_p ·····Isopropylidene group
a ·····Compounds of D-series
b ·····Compounds of L-series
c ·····The epimer of a



—| Acetyl group
—Ts *p*-toluenesulfonyl group



1) J. Yoshimura and T. Sata, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **80**, 1479 (1959).
2) R. Kuhn and W. Kirschenlohr, *Ann.*, **600**, 115 (1956).
3) K. Gätzi and V. T. Reichstein, *Helv. Chim. Acta.*, **21**, 914 (1938) ; J. English, Jr. and P. H. Griswold,Jr., *J. Am. Chem. Soc.*, **67**, 2039 (1945).
4) C. S. Hudson, **41**, 1141 (1919).
5) W. E. Glattfeld and D. Macmillan, **56**, 2481 (1934).

Table I. Results of periodate oxidation experiments

Compounds	Mol. of periodate consumed/mol. of compds.				Mol. of formaldehyde liberated
	1 hr.	2 hr.	3 hr.	9 hr.	
I[a]	3.50	3.53	3.69	3.80	1.07
II[a]	1.70	1.70	1.92	2.20	0.02
III[b]	0.00	0.00	0.00	0.00	—
IV[b]	0.85	0·89	0.93	1.09	1.02
IX	0.00	0.00	0.00	0.26	—
X	0.00	0.00	0.00	0.00	—
XV	1.82	1.85	1.90	2.13	0.03
XVI	1.93	1.97	2.15	2.35	—

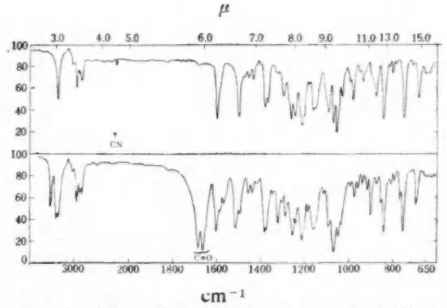


Fig. 1. The infrared specta of III[a] and IX[b].

hydrolysis of organic nitriles[6] to acidamides in alkalline hydrogen peroxide was applied to the above isopropylidene glucosaminonitriles. III[a] and III[b] are successfuly hydrolyzed to the corresponding glucosaminic acidamide (IX[a] and IX[b]) in good yield, though II[a] or IV[a] does not afford a crystalline product. The infrared spectra (Fig. 1) show the absorption peak of nitrile (4.5 μ) in III[a] but not in IX[b], while as for the carbonyl peaks (5.94, 6.01 μ) the condition is vice versa.

Different from the corresponding *N*-methyl[7] and *N*-benzyl[2] derivatives, acetylation of I[b] with acetic anhydride in pyridine affords the corresponding tetra-*O*-acetate (X) in which the hydrogen atom attached to nitrogen is not being replaced by an acetyl group. Tosylation of I[b] in pyridine led to the crystalline 6-*O*-*p*-toluenesulfonyl derivative (XI), which is acetylated to the corresponding 3, 4, 5-tri-*O*-acetyl derivative (XII), and the position of *p*-toluenesulfonyl group was confirmed by conversion to the 6-iodo derivative (XIII).

Periodate oxidation of these derivatives (Table I) shows that a nitrile group does not consume the periodate as a mercaptal group[1,8] does, and nitriles having the unprotected hydroxyl group at carbon 3 (adjacent to amino group) are over-oxidized similarly to that of mercaptals[1].

There are a few examples[2,9] in which the reactivity of glucosaminonitrils are different with *N*-substituted groups. Thus, the reaction of *N*-benzyl-L-glucosaminonitrile (XIV) with acetone in the presence of concentrated sulfuric acid does not lead to the corresponding isopropylidine derivative, but crystalline 5, 6-*O*-isopropylidene-*N*-bynzyl-L-glucosaminic acid amide (XV) and 5, 6-*O*-isopropylidene-*N*-benzyl-L-glucosaminic acid, (XVI) in which the position of these isopropylidene groups was deduced from the results of periodate oxidation in Table I, were separated by chromatography of the reaction product on a magnesol-celite column. These aspects are now under investigation.

Experimental

5, 6-*O*-Isopropylidene-*N*-phenyl-D-glucosaminonitrile (II[a]).—(i) A mixture of 1 g. of *N*-phenyl-D-glucosaminonitrile (I[a]), 30 ml. of anhydrous acetone and 4 g. of anhydrous cupric sulfate was stirred at 37~40°C for 6 hr., and the acetone solution separated from solids was concentrated in vacuo. The residual sirup crystallized on scratching with a little amount of ether was recrystallized twice from ethanol-petrolum ether; m. p. 124~5°C. Yield, 0.8 g. $[\alpha]_D^{26}+141°$ (*c* 0.82, methanol).

Found: C, 61.55; H, 7.02; N, 9.54. Calcd. for $C_{15}H_{20}O_4N_2$ (292.3): C, 61.63; H, 6.90; N, 9.58%.

(ii) To a mixture of 9.0 g. of 5, 6-*O*-isopropylidene-D-arabinose diethylmercaptal (V) in 50 ml. of acetone and 70 g. of moist cadmium carbonate was added a solution of 30 g. of mercuric chloride in 40 ml. of acetone and the mixture was vigorously stirred for 4 hr. at room temperature. 20 g. of moist cadmium carbonate was again added, and then heated at 50°C for 1 hr. The reaction mixture was cooled, diluted with acetone, filtered and the solid was washed with the same solvent. After complete removal of acetone from the combined filtrate and washings at room temperature in the presence of cadmium carbonate, the mixture was extracted with chloroform and the extract dried with sodium

6) R. H. Wiley and H. S. Morgan, Jr., *J. Org. Chem.*, **15**, 800 (1950); J. V. Murray and J. B. Cloke, *J. Am. Chem. Soc.*, **56**, 2749 (1934).
7) M. L. Wofrom, A. Thompson and I. R. Hooper, *J. Am. Chem. Soc.*, **68**, 2343 (1946).
8) L. Hough and M. I. Taha, *J. Chem. Soc.*, **1956**, 2042.
9) R. Kuhn and W. Bister, *Ann.*, **602**, 217 (1957).

sulfate. A pale yellow sirup (2.5 g.) remained by evaporation of the solvent was dissolved in 4 ml. of ethanol, and 1 ml. of aniline and 1.5 ml. of ethanol, and 1 ml. of aniline and 1.5 ml. of hydrogen cyanide was added. After being kept in the refrigerator for 3 hr., the mixture was concentrated to dryness in vacuo, and the residual syrup was dissolved in ethanol-petroleum ether. The solution was seeded with II[a] and stored in the refrigerator overnight and 0.8 g. of crystals, m. p. 123~5°C, was yielded. These showed no depression on admixture with II[a].

5, 6-*O*-Isopropylidene-*N*-phenyl-L-glucosaminonitrile (II[b]).—0.8 g. of *N*-phenyl-L-glucosaminonitrile (I[b]) was treated in exactly the same manner as in the case of II[a], and 0.6 g. of colorless needles was obtained, m. p. 124~5°C. $[\alpha]_D^{25}$ −138° (*c* 0.70, methanol).

Found: C, 61.66; H, 7.05; N, 9.60. Calcd. for $C_{15}H_{20}O_4N_2$ (292.3): C, 61.63; H, 6.90; N, 9.58%.

3, 4; 5, 6-Di-*O*-isopropylidene-*N*-phenyl-D-glucosaminonitrile (III[a]).—To a mixture of 3 g. of I[a] and 60 ml. of anhydrous acetone, 1.6 ml. of concentrated sulfuric acid was added dropwise. After standing at room temperature for 4 hr., the slightly colored clear solution was poured into an excess amount of saturated aqueous solution of sodium carbonate in cooling, and filtered. The filtrate was extracted with chloroform used for washing the filtered sodium sulfate, and the extract was washed with water and dried with anhydrous sodium sulfate. The colorless crystals obtained by evaporation of the chloroform extract were recrystallized twice from ethanol: m. p. 106~8°C, Yield 2.5 g., $[\alpha]_D^{26}$ +140° (*c* 0.37, methanol.)

Found: C, 64.74; H, 7.27; N, 8.50. Calcd. for $C_{15}H_{24}O_4N_2$ (332.4): C, 65.04; H, 7.28; N, 8.43%.

Reaction of 2, 3; 4, 5-Di-*O*-isopropylidene-aldehydo-D-arabinose (VII), Aniline and Hydrogen Cyanide.—To a solution of 15 ml. of absolute ethanol and 9 g. of VII (b. p. 182~3°C/0.35 mmHg) were added 5 ml. of aniline and 10 ml. of anhydrous hydrogen cyanide. After being kept overnight in the refrigerator, the solution was concentrated in vacuo to a sirup, which was crystallized on scratching with a small amount of petroleum ether, and recrystallized from ethanol; yield 9 g., m. p. 106~8°C. $[\alpha]_D^{25}$ +138° (*c* 2.0, methanol). These showed no depression on admixture with III[a]. 3, 4; 5, 6-Di-*O*-isopropylidene-*N*-phenyl-D-mannosaminonitrile obtained from the above mother liquor by concentration was recrystallized twice from ether-petrolum ether; yield 3 g., m. p. 93~5°C. $[\alpha]_D^{26}$ +12.8° (*c* 0.35, methanol).

Found: C, 64.97; H, 7.50; N, 8.36. Calcd. for $C_{15}H_{24}O_4N_2$ (332.4): C, 65.04; H, 7.28; N, 8.43%.

3, 4-*O*-Isopropylidene-*N*-phenyl-D-glucosaminonitrile (IV[a]).—(i) A mixture of 2 g. of III[a] in acetone (65%, 50 ml.) and aqueous sulfuric acid (6 N, 10 ml.) was warmed at 45~55°C for 40 min., and then poured into an excess amount of saturated sodium bicarbonate solution under cooling; it was then filtered. The residue was washed with chloroform, and the filtrate was extracted with the washings. The chloroform extract was washed with water and dried with anhydrous sodium sulfate, and evaporated in vacuo. The residual syrup was crystallized from ether-petroleum ether; m. p. 97~9°C. Yield 1.2 g. $[\alpha]_D^4$ +75.6° (*c* 0.79, methanol).

Found: C, 61.46; H, 7.38; N, 9.52. Calcd. for $C_{15}H_{20}O_4N_2$ (292.3): C, 61.63; H, 6.90; N, 9.58%.

(ii) Freshly precipitated moist cadmium carbonate, 90 g. was heated rapidly to 50°C in a solution of 10.5 g. of 2, 3-*O*-isopropylidene-D-arabinose diethylmercaptal in 55 ml. of acetone with vigorous stirring in nitrogen atmosphere. As soon as 50°C was reached 40 g. of mercuric chloride in 50 ml. of acetone was added over a period of 10 min. and stirring continued at 50°C for further 5 min. The mixiure was immediately cooled, diluted with acetone, centrifuged and washed on the centrifuge with the same solvent. After complete removal of acetone from the combined filtrate and washings at room temperature in the presence of fresh cadmium carbonate, the mixture was extracted with chloroform and the extract dried with sodium sulfate. Evaporation of the solvents gave 2 g. of pale yellow sirup. This syrup was dissolved in 5 ml. of ethanol with 1 g. of aniline and 1 ml. of anhydrous hydrogen cyanide, and left to stand for 3 hr. at room temperature. The mixture was concentrated in vacuo to a sirup, again dissolved in 5 ml. of ethanol, and water was added just before clouding took place at 40°C. A little amount of syrup separated was decanted at room temperature and the clear solution was stored in the refrigerator overnight. The crystals separated were collected and recrystallized from ethanol-water, m. p. 97~9°C. Yield 0.6 g. These showed no depression on admixture with IV[a].

3, 4-*O*-Isopropylidene-*N*-phenyl-L-glucosaminonitrile (IV[b]).—In exactly the same manner in the case of IV[a], 1.3 g. of crystals was obtained from 2 g. of III[b]. It was recrystallized from aqueous ethanol, m. p. 97~9°C, $[\alpha]_D^{26}$ −78.3° (*c* 0.97, methanol).

Found: C, 61.34; H, 7.28; N, 9.54. Calcd. for $C_{15}H_{20}O_4N_2$ (292.3): C, 61.63; H, 6.90; N, 9.58%.

2, 3-*O*-Isopropylidene-D-arabinose Diethylmercaptal (VIII).—A mixture of 16 g. of 2, 3; 4, 5-di-*O*-isopropylidene-D-arabinose diethylmercaptal in acetone (90 ml.) and aqueous sulfuric acid (6 N, 18 ml.) was heated at 45~50°C for 20 min. The solution was poured into an excess amount of cold saturated sodium bicarbonate solution and filtered. The residue was washed with chloroform, and the filtrate was extracted with washings. The chloroform extract was washed, dried and concentrated in the usual manner. By fractional distillation of the residue was obtained 10.4 g. of colorless syrup; b. p. 140°C/0.07 mmHg, 150~1°C/0.3 mmHg. $[\alpha]_D^6$ +86.2° (*c* 0.44, methanol).

Found: C, 48.94; H, 8.39; S, 21.23. Calcd. for $C_{12}H_{24}O_4S_2$ (296.4): C, 48.62; H, 8.16; S, 21.63%.

2, 3; 4, 5-Di-*O*-isopropylidene-*N*-phenyl-D-glucosaminic Acidamide (IX[a]).—A mixture of 2 g. of III[a], 35 ml. of acetone, hydrogen peroxide (30%, 7 ml.), sodium carbonate (10%, 3 ml.) and 18 ml. of water was refluxed 80 min. on a steam bath, and acetone was then removed in vacuo. The remained mixture of crystalline substances and water was extracted with chloroform in the usual

manner. The crystals obtained by evaporation of solvents in vacuo were recrystallized from ethanol; yield, 1.4 g., m. p. 147~8°C. $[\alpha]_D^{25}$ −5.1° (*c* 0.33, methanol).

Found: C, 61.40; H, 7.56; N, 8.00. Calcd. for $C_{15}H_{23}O_5N_3$ (350.4): C, 61.70; H, 7.48; N, 8.00%.

2, 3, 4, 5-Di-*O*-isopropylidene-*N*-phenyl-L-glucosaminic Acidamide (IX[b]).—In exactly the same manner in the case of IX[a], 3.5 g. of crystals was obtained from 5 g. of III[b]. It was recrystallized from ethanol-petroleum ether, m. p. 146~8C. $[\alpha]_D^{26}$ −4.5° (*c* 1.81, methanol).

Found: C, 61.80; H, 7.66; N, 7.17. Calcd. for $C_{15}H_{26}O_5N_2$ (350.4): C, 61.70; H, 7.48; N, 8.00%.

3, 4, 5, 6-Tetra-*O*-acetyl-*N*-phenyl-L-glucosaminonitrile (X).—To a solution of 3 g. of I[b] in 16 ml. of dry pyridine, 15 ml. of acetic anhydride was added under cooling, and the mixed solution was left to stand for 24 hr. at room temperature. The reaction mixture was then poured into ice-water and extracted with chloroform in the usual manner. The extract was evaporated to dryness, and the residue was crystallized from ethanol. Yield 3.2 g., m. p. 127~8°C. $[\alpha]_D^{25}$ −83.5° (*c* 0.55, methanol).

Found: C, 56.59; H, 5.99; N, 6.82. Calcd. for $C_{20}H_{24}O_8N_2$ (420.6): C, 57.13; H, 5.75; N, 6.66%.

6-*O*-(*p*-Toluenesulfonyl)-*N*-phenyl-L-glucosaminonitrile (XI).—To a solution of 2 g. of I[b] in 10 ml. of dry pyridine, a solution of 1 g. of *p*-toluenesulfonylchloride in 5 ml. of dry pyridine was added under cooling. After standing overnight at room temperature, the reaction mixture was poured into ice-water and extracted with chloroform. In the course of washing the extracts with 1 N sulfuric acid crystalls precipitated, and these were collected and recrystallized from ethanol. Yield, 1.5 g., m. p. 131~4°C, $[\alpha]_D^{25}$ −96.5° (*c* 0.96, methanol).

Found: C, 56.48; H, 5.71, N, 6.87; S, 7.55. Calcd. for $C_{19}H_{22}O_6N_2S$ (406.5): C, 56.15; H, 5.46; N, 6.89; S, 7.89%.

3, 4, 5-Tri-*O*-acetyl-6-*O*-(*p*-toluenesulfonyl)-*N*-phenyl-L-glucosaminonitrile (XII).—A mixture of 3 g. of XI, 20 ml. of acetic anhydride and 20 ml. of dry pyridine was left to stand overnight at room temperature and then poured into ice-water. The solution was extracted with chloroform in the usual manner. The crystals obtained by evaporation of the solvent was recrystallized from ethanol; yield. 2.9 g., m. p. 132~4°C., $[\alpha]_D^{25}$ −62.5° (*c* 0.28, methanol).

Found: C, 56.54; H, 5.50; N, 5.26; S, 5.85. Calcd. for $C_{25}H_{29}O_9N_2S$ (532.6): C, 56.38; H, 5.30; N, 5.26; S, 6.02%.

3, 4, 5-Tri-*O*-acetyl-6-iodo-*N*-phenyl-L-glucosaminonitrile (XIII).—In a glass tube 2 g. of XII. 0.56 g. of sodium iodide and 40 ml. of dry acetone were sealed and heated in a steam bath for 1 hr. Sodium *p*-toluenesulfonate separated (0.69 g., 95% of the theoretical amount) was filtered off. The filtrate was evaporated to dryness in vacuo, and the residue was extracted with chloroform in the usual manner. Evaporation of the extracts afford 1.6 g. of pale yellow syrup, which could not crystallize or distill for purification. $[\alpha]_D^{25}$ −51.5° (*c* 0.55, methanol).

Found: C, 44.73; H, 4.68; N, 6.06; I, 25.18. Calcd. for $C_{15}H_{21}O_6N_2I$ (488.3): C, 44.27; H, 4.33; N, 5.74; J, 25.99%.

Reaction of *N*-benzyl-L-glucosaminonitrile (XV) and Acetone in the Presence of Concentrated Sulfuric Acid.—A mixture of 10 g. of XV, 200 ml. of anhydrous acetone and 5 ml. of conc. sulfuric acid was stirred at room temperature for 4 hr. The brown reaction mixture was treated similarly to that the case of III[a]. The crude syrup (9 g.) was fractionated on a magesol-celite column (25 g. of 1:5 mixture) with every 100 ml. of the solvent; (1) benzene-petroleum ether (1:1), (2) benzene-petroleum ether (2:1), (3) benzene, (4) benzene-ethanol (2:1), (5) benzene-ethanol (1:2) as mobile phase.

Fraction 3 gave needles of 5,6-*O*-isopropylidene-*N*-benzyl-L-glucosaminic acid (0.5 g.) which were recrystallized from ethanol, m. p. 192~3°C decomp., $[\alpha]_D^5$ −165° (*c* 0.2, methanol).

Found: C, 59.10; H, 7.36; N, 4.35. Calcd. for $C_{16}H_{23}O_6N$ (325.3): C, 59.06; H, 7.13; N, 4.31%.

Fraction 4 gave crystals of 5,6-*O*-isopropylidene-*N*-benzyl-L-glucosaminic acidamide (2.0 g.) which were recrystallized from ethanol-ether, m. p. 163~4°C, $[\alpha]_D^4$ −42.5° (*c* 0.65, methanol).

Found: C, 58.89; H, 7.35; N, 8.70. Calcd. for $C_{16}H_{24}O_5N_2$ (324.4): C, 59.24; H, 7.46; N, 8.64%.

Periodate Oxidation Experiments.—In each case, a mixture of 0.2 M-sodium periodate (5 ml.) and the compound (25~30 mg. accurately weighed) and 4 ml. of ethanol was made up to 25 ml. with water and stored in a refrigerator. A blank containing none of the compound was worked concurrently. At intervals, the periodate uptake was estimated by transferring sample (2 ml.) from the oxidation mixture and the blank into mixtures of phosphate buffer (pH 6.98; 25 ml.) and 20% potassium iodate solution (1 ml.), and the liberated iodine titrated with 0.01 N sodium thiosulfate solution, starch being used as indicator[10]. Formaldehyde was determined colorimetrically with chromotropic acid according to O'Dea and Gibbon's method[11], D-glucose being used as standard.

The author wishes to express his hearty thanks to Professor T. Sato, Tokyo Institute of Technology, for his encouragement throughout this work.

Laboratory of Organic Chemistry
Tokyo Institute of Technology
Meguro-ku, Tokyo

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The Thermal Decomposition of Acetaldehyde in the Presence of Methanethiol

By Naomi IMAI and Osamu TOYAMA

(Receiced April 16, 1960)

It is well known that reactions between thiols and free redicals, and between organic compounds and thiol radicals occur easily compared to other radical-molecule reactions. But only a few kinetic studies about these reactions are found in the literature[1,2]. The present authors have recently studied the photochemical[3] as well as the thermal[4] decomposition of acetaldehyde in the presence of hydrogen sulfide. These studies have shown that the chain decomposition of acetaldehyde is catalyzed by hydrogen sulfide, and this catalytic effect has been attributed to a chain mechanism involving reactions between methyl radical and hydrogen sulfide and between hydrosulfide radical and acetaldehyde. In a mixture of acetaldehyde and a thiol, a similar catalysis may be expected to take place. In this work a kinetic study of the thermal decomposition of acetaldehyde in the presence of methanethiol has been carried out to obtain information on elementary reactions involving methanethiol or its radical.

Experimental

Materials.—Acetaldehyde was prepared by distillation of paraldehyde containing a small quantity of sulfuric acid and purified by bulb-to-bulb distillation. Methanthiol was obtained[5] by adding a sodium hydroxide solution to *S*-methyl isothiourea sulfate, which was prepared by the reaction between dimethyl sulfate and thiourea. It was then passed through a trap containing concentrated sulfuric acid and through a tower containing dry calcium chloride, and finally purified by bulb-to-bulb distillation.

Apparatus.—The thermal decomposition was carried out in a cylindrical glass vessel of 137 cc. placed in an electric furnace. The reaction vessel was connected to a mercury manometer, to an analytical system, to storage bulbs and to a bulb in which acetaldehyde and methanethiol were mixed before they were admitted to the reaction vessel. The reaction vessel, the manometer, the bulbs for storage and mixing and the analytical system were all attached to a conventional vacuum line.

Procedure.—Required quantities of acetaldehyde and methanethiol were admitted into the mixing bulb at room temperature and left for about 30 minutes to allow them to mix thoroughly. The mixed reactant gases were then introduced into the reaction vessel, which had already been kept at the experimental temperature, and the change in the total pressure with time was followed on a manometer. The products of decomposition in several runs were analyzed quantitatively in the same way as described previously[6].

Results

It has been established by many workers that the products of the thermal decomposition of acetaldehyde are almost exclusively equal quantities of methane and carbon monoxide[7]. Similarly in this work, i.e., in the presence of methanethiol, it has been confirmed by analysis that the rate of formation of methane is identical with that of carbon monoxide, and the pressure of either one of these products corresponds to the total pressure increase within the experimental error. Thus, irrespective of the presence of methanethiol, the total pressure increase is always equal to the decrease in the pressure of acetaldehyde due to decomposition. Accordingly, the initial rate of decomposition was determined from the initial slope of a total pressure-time curve with the results shown in Figs. 1 and 3 and Table I. Fig. 1 shows the dependence of the rate of decomposition on the pressure of acetaldehyde in the experiments with acetaldehyde alone. Table I and Fig. 3 show the dependence of the rate of decomposition in the presence of methanethiol on the pressures of methanethiol and of acetaldehyde, respectively.

Discussion

It is generally agreed that the main feature of thermal decomposition of acetaldehyde can

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2) J. A. Kerr and A. F. Trotman-Dickenson, ibid., **1957**, 3322.
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6) N. Imai and O. Toyama, This Bulletin, 33, 652 (1960).
7) C. J. M. Fletcher and C. N. Hinshelwood, *Proc. Roy. Soc.* (London), **A141**, 41 (1933); C. A. Winkler and C. N. Hinshelwood, ibid., **A149**, 355 (1935); R. V. Seddon and M. W. Travers, ibid., **A156**, 234 (1936); E. Leifer and H. C. Urey, *J. Am. Chem. Soc.*, **64**, 994 (1942).

TABLE I. EFFECT OF METHANETHIOL ON THE PYROLYSIS OF ACETALDEHYDE
Initial pressure of CH_3CHO, 100 mmHg

400°C		420°C		440°C	
Initial press. of CH_3SH (mmHg)	Initial rate of decomp. (mmHg/min.)	Initial press. of CH_3SH (mmHg)	Initial rate of decomp. (mmHg/min.)	Initial press. of CH_3SH (mmHg)	Initial press. of decomp. (mmHg/min.)
0.63	0.40	5.8	2.1	5.8	4.7
1.0	0.50	9.2	2.5	6.9	4.8
3.3	0.64	10.5	2.6	9.5	5.1
3.5	0.77	11.8	2.8	11.1	5.6
5.3	0.88	14.6	2.9	12.3	5.6
8.4	1.04	14.8	3.2	13.6	6.1
13.3	1.32	23.0	3.4	14.8	6.4
15.0	1.4	25.5	3.6	20.0	6.7
20.0	1.6	29	3.9	22.1	7.2
21.3	1.7	33	4.0	24	7.5
21.4	1.7	36	4.4	26	8.0
34	2.0	58	5.4	35	8.2
42	2.3	71	6.0	47	9.8
67	2.7	85	6.7	55	10.4
88	3.1				

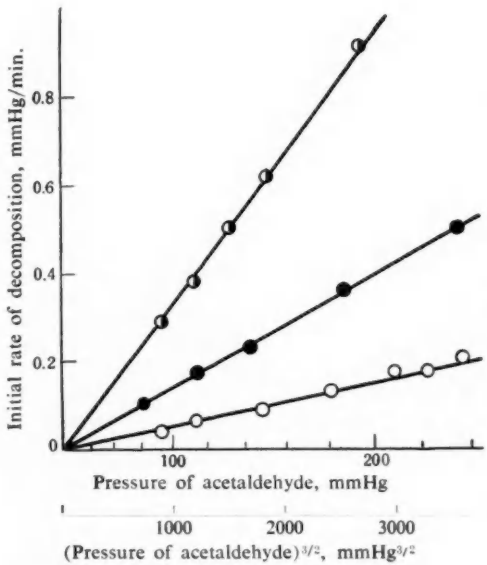

Fig. 1. Rate of decomposition of acetaldehyde alone. ○, 400; ●, 420; ◑, 440°C.

be explained by the following mechanism[8]

$$CH_3CHO = CH_3 + CHO \quad (1)$$

$$CHO = CO + H \quad (2)$$

$$H + CH_3CHO = H_2 + CH_3CO \quad (3)$$

$$CH_3CO = CH_3 + CO \quad (4)$$

$$CH_3 + CH_3CHO = CH_4 + CH_3CO \quad (5)$$

$$CH_3 + CH_3 = C_2H_6 \quad (6)$$

The steady state equations derived from this scheme yield the rate equation

$$-d[CH_3CHO]/dt = k_1^{1/2}k_5\,k_6^{-1/2}[CH_3CHO]^{3/2} \quad (I)$$

in general agreement with experimental results obtained by various workers. Also in this work, the rate of decomposition was found to be proportional to the 3/2 power of the pressure of acetaldehyde as seen in Fig. 1. From the slopes of the straight lines in the figure, the value of $k_1^{1/2}k_5\,k_6^{-1/2}$ at each temperature was obtained and listed in Table II.

TABLE II. VALUES OF $k_1^{1/2}k_5k_6^{-1/2}$, $k_1k_{11}^2k_{12}^{-1}$ AND $k_7k_{11}^2k_{12}^{-1}$

Temp. (°C)	$k_1^{1/2}k_5k_6^{-1/2}$ ($mol^{-1/2}$ $cc^{1/2}$ $sec^{-1/2}$)	$k_1k_{11}^2k_{12}^{-1}$ (mol^{-1} cc sec^{-1})	$k_7k_{11}^2k_{12}^{-1}$ (mol^{-1} cc sec^{-1})
400	0.045	0.245	7.4
420	0.116	1.40	33
440	0.28	7.4	141

Now in the presence of methanethiol, the additional possibilities may be[9]

$$CH_3SH = CH_3 + SH \quad (7)$$

$$SH + CH_3SH = H_2S + CH_3S \quad (8)$$

8) F. O. Rice and K. F. Herzfeld, *J. Am. Chem. Soc.*, **56**, 284 (1934); E. W. R. Steacie, "Atomic and Free Radical Reaction", 2nd Ed., Reinhold Publ. Corp., New York, (1954), p. 206.

9) Reactions similar to 10, 11 and 12 have been proposed by the following workers: E. F. P. Harris and W. A. Waters, *Nature*, **170**, 212 (1952); K. E. J. Banett and W. A. Waters, *Discussions Faraday Soc.*, **14**, 221 (1953); Ref. 1.

$$SH + CH_3CHO = H_2S + CH_3CO \quad (9)$$

$$CH_3 + CH_3SH = CH_4 + CH_3S \quad (10)$$

$$CH_3S + CH_3CHO = CH_3SH + CH_3CO \quad (11)$$

$$CH_3S + CH_3S = \text{Product} \quad (12)$$

Sehon and Darwent[10] suggest that in the thermal decomposition of methanethiol the split of C–S bond, and not that of S–H, takes place, in view of the fact that major products found by using toluene as a carrier are methane, hydrogen sulfide and dibenzyl. Their suggestion seems reasonable judging from the dissociation energies of C–S and S–H bonds of methanethiol which have been estimated as 74.2 and 88.8 kcal./mol., respectively[11]. Skerrett and Thompson[12] have shown that the product of reaction 12 is mainly methyl disulfide $(CH_3)_2S_2$ by analysis of the products obtained in the photolysis of methanethiol, where the primary reaction is the split of S–H bond of the methanethiol molecule that absorbed light.

When reactions 10 and 11 are much faster than reaction 5, acetaldehyde decomposes mostly by a chain mechanism consisting of reactions 10, 11 and 4. If, in addition, reaction 10 is faster than reaction 11, the concentration of methylthio radicals will be greater than that of methyl radicals and reaction 12. These assumptions lead to the following rate equation.

$$-\mathrm{d}[CH_3CHO]/\mathrm{d}t = k_{11}k_{12}^{-1/2}(k_1[CH_3CHO] + k_7[CH_3SH])1/2[CH_3CHO] \quad (II)$$

or

$$(-\mathrm{d}[CH_3CHO]/\mathrm{d}t)^2 = k_{11}^2k_{12}^{-1}(k_1[CH_3CHO]^3 + k_7[CH_3CHO]^2[CH_3SH]) \quad (III)$$

As seen in Fig. 2, except in a low pressure range of methanethiol, the square of the rate of decomposition increases linearly with the pressure of methanethiol in agreement with equation III. At lower pressures of methanethiol, the relative concentration of methylthio radicals to that of methyl radicals falls off and consequently the importance of the recombination of methyl radicals becomes greater. This explains the deviation from equation III at

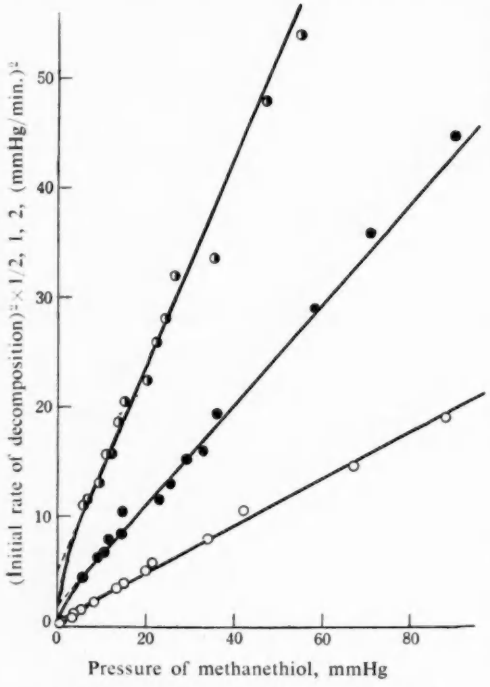

Fig. 2. Dependence of the rate of decomposition in the presence of methanethiol on its pressure. CH_3CHO: 100 mmHg. ○, (Rate)²×2, 400°C; ●, (Rate)²×1, 420°C; ◑, (Rate)²×1/2, 440°C.

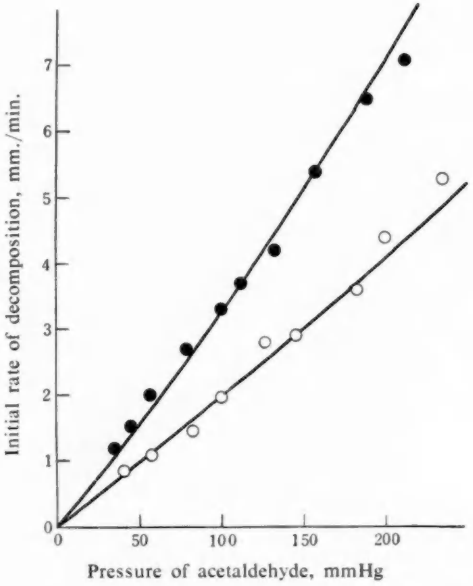

Fig. 3. Dependence of the rate of decomposition in the presence of methanethiol on acetaldehyde pressure. ○, CH_3SH: 33 mmHg, 400°C; ●, CH_3SH: 19 mmHg, 420°C. Circles and full lines represent observed and calculated rates, respectively.

10) A. H. Sehon and B. Darwent, *J. Am. Chem. Soc.*, **76**, 4806 (1954).
11) J. L. Franklin and H. E. Lumpkin, ibid., **74**, 1023 (1952).
12) N. D. Skerrett and N. W. Thompson. *Trans. Faraday Soc.*, **37**, 81 (1941).

low pressures of methanethiol. From the intercepts and slopes of the straight lines in Fig. 2 values of $k_1k_{11}^2k_{12}^{-1}$ and $k_7k_{11}^2k_{12}^{-1}$ are obtained, which are listed in Table II together with values of $k_1^{1/2}k_5k_6^{-1/2}$ already mentioned above.

Fig. 3 shows the plots of the rate of decomposition observed at a constant pressure of methanethiol against the pressure of acetaldehyde, together with the curves representing the rate calculated as a function of acetaldehyde pressure by equation II using the values of $k_1k_{11}^2k_{12}^{-1}$ and $k_7k_{11}^2k_{12}^{-1}$ given in Table II. The fact that the calculated curves are in satisfactory agreement with the experimental plots over a wide range of acetaldehyde pressure may be taken as an additional evidence for the validity of equation II.

The values given in Table II lead to the following Arrhenius expressions:

$$k_1^{1/2}k_5k_6^{-1/2}=10^{12.8}\exp(-43{,}500/\boldsymbol{RT})$$
$$(\mathrm{mol}^{-1/2}\ \mathrm{cc}^{1/2}\ \mathrm{sec}^{-1/2})$$
$$k_1k_{11}^2k_{12}^{-1}=10^{25.8}\exp(-81{,}300/\boldsymbol{RT})$$
$$(\mathrm{mol}^{-1}\ \mathrm{cc.}\ \mathrm{sec}^{-1})$$
$$k_7k_{11}^2k_{12}^{-1}=10^{23.7}\exp(-70{,}200/\boldsymbol{RT})$$
$$(\mathrm{mol}^{-1}\ \mathrm{cc.}\ \mathrm{sec}^{-1})$$

The expression for $k_1^{1/2}k_5k_6^{-1/2}$ agrees with those reported previously by various workers. Combining the expression for $k_1^{1/2}k_5k_6^{-1/2}$ with that for $k_1k_{11}^2k_{12}^{-1}$, we obtain

$$(k_5/k_{11})(k_{12}/k_6)^{1/2}=0.8\exp(-2{,}800/\boldsymbol{RT})$$

If we assume that k_{12} has zero activation energy and a pre-exponential factor of the same value as that of k_6, the left-hand side of the equation becomes equal to k_5/k_{11}. The difference in activation energies $E_5-E_{11}=2.8$ kcal./mol. thus obtained compares with 1.6 kcal./mol. obtained by Birrel et al.[1] in the photolysis of mixtures of acetaldehyde and methanethiol. The value of the ratio $A_5/A_{11}=0.8$ also seems reasonable, as pre-exponential factors of these two reactions are expected to be of the same order of magnitude.

From the expressions for $k_1k_{11}^2k_{12}^{-1}$ and $k_7k_{11}^2k_{12}^{-1}$ given above, it follows that

$$k_1/k_7=130\exp(-11{,}100/\boldsymbol{RT})$$

The difference in activation energies $E_1-E_7=11$ kcal./mol., when combined with $E_1=75$ kcal./mol., yields a value of 64 kcal./mol. for E_7. Franklin and Lumpkin[11] estimated the dissociation energy of C-S bond in methanethiol to be 74.2 kcal./mol. by an electron impact method. Sehon and Darwent[10] obtained a lower dissociation energy of 67 kcal./mol. from the rates of decomposition of methanethiol in the presence of toluene as a carrier, assuming a pre-exponential factor of 3×10^{13} sec^{-1}. The value of 64 kcal./mol. obtained above in the present work is still lower than that of Sehon and Darwent. As can be seen in Fig. 2, the straight lines representing the square of the rate of decomposition as a function of acetaldehyde pressure cut the ordinate axis very close to the origin. Hence the values of the intercept and consequently the expression for k_1/k_7 given above must be accepted with some reserve. In fact, a value of the ratio A_1/A_7 amounting to 1.3×10^2 may be too large. If this ratio has really a smaller value, E_7 is greater than the value estimated above; if A_1/A_7 is put equal to unity, E_7 becomes as large as 70 kcal./mol.

As has been shown above, the results obtained in the present work comform to equation II based upon a mechanism in which the reaction chain terminates by the combination of methylthio radicals, while, in the photochemical[3] and thermal[3] decomposition of acetaldehyde in the presence of hydrogen sulfide, the experimental results indicate that the chain terminates by the combination of methyl radicals and not of hydrosulfide radicals. In these decomposition reactions, factors determining the chain-ending step may be the concentration ratio $[RS]/[CH_3]$, where R represents CH_3 or H, and the relative abilities of radicals to recombine. The former quantity in the steady state is given by $k_A[RSH]/k_B[CH_3CHO]$ where k_A and k_B are respectively the specific rates of the following reactions:

$$CH_3 + RSH = CH_4 + RS \qquad (A)$$
$$RS + CH_3CHO = RSH + CH_3CO \qquad (B)$$

Although our experimental results indicate that the activation energy of reaction A, E_A, is lower than E_B for hydrogen sulfide, and that $k_A=10^{11.4}\exp(-2{,}600/\boldsymbol{RT})$ mol^{-1}[6] cc. sec^{-1} for hydrogen sulfide and E_B is around 4 kcal./mol. methanethiol, we are yet given no complete expressions for all the k_A's and k_B's at present and accordingly cannot compare the value of the ratio $[RS]/[CH_3]$ for methanethiol with that for hydrogen sulfide. If, however, these values were of comparable magnitudes in these experiments, the difference between the chain-ending steps in the experiments with methanethiol and with hydrogen sulfide would mean the lower ability of hydrosulfide radicals to recombine, compared to that of methylthio radicals.

It has been found in the present work that the rate of decomposition falls off during a run faster than can be expected from the rate equation. The higher are the pressure of methanethiol and the temperature, the greater is the extent of this reduction in the rate. Similar

phenomena have been observed in the photolysis of acetaldehyde in the presence of hydrogen sulfide[3]. The exact nature of these phenomena are not clear at present.

Summary

Acetaldehyde has been decomposed thermally in the presence of methanethiol over the temperature range from 400° to 440°C. The presence of methanethiol markedly enhances the rate of decomposition. Analysis of the initial rates of decomposition obtained under various experimental conditions suggests: a) one of the chain-carrying steps $CH_3+CH_3CHO=CH_4+CH_3CO$ (5) in the decomposition of acetaldehyde alone is replaced by $CH_3+CH_3SH=CH_4+CH_3S$ (10) and $CH_3S+CH_3CHO=CH_3SH+CH_3CO$ (11) in the presence of methanethiol; b) the reaction $CH_3SH=CH_3+SH$ (7), in addition to $CH_3CHO=CH_3+CHO$ (1), contributes to the chain initiation; c) the chain terminates by the combination of methylthio radicals in contrast to the decomposition in the presence of hydrogen sulfide where the chain-ending step is the combination of methyl radicals under similar experimental conditions; d) $k_5/k_{11}=0.8\exp(-2{,}800/RT)$ and $k_1/k_7=130\exp(-11{,}000/RT)$, the latter expression being less certain.

The present study was partly supported by the finantial aid of the Ministry of Education, to which the authors' thanks are due.

Department of Applied Chemistry
College of Engineering
University of Osaka Prefecture
Sakai, Osaka

The Formation Constants of Metal Acetate Complexes. III. Polarographic Determination of the Formation Constants of Acetatocadmium(II) and Acetatocobalt(II) Complexes

By Nobuyuki TANAKA, Minoru KAMADA, Hisao OSAWA and Gen SATÔ

(Received May 18, 1960)

In the previous papers[1,2], the formation constants of acetato complexes of nickel(II), copper(II), lead(II) and zinc(II) were reported. They were determined by the newly devised methods, which are based on the polarographic measurement of the sum of the equilibrium concentrations of hydrated metal ions and metal acetate complexes. In the case of acetatocopper(II), acetatolead(II) and acetatozinc(II) complexes, the substitution reaction of the type,

$$M^{m+}+M'Y^{(m'-4)+} \rightleftarrows MY^{(m-4)+}+M'^{m'+} \quad (1)$$

where Y^{4-} means a completely dissociated ethylenediaminetetraacetate(EDTA) anion, was used for the determination of the formation constants. This was based on the fact that, in acetate buffers, the substitution reaction (Eq. 1) was considered to be

$$\left\{\begin{matrix}M^{m+}\\ \uparrow\downarrow\\ M(OAc)_n^{(m-n)+}\end{matrix}\right\}+\left\{\begin{matrix}M'Y^{(m'-4)+}\\ \uparrow\downarrow\\ M'HY^{(m'-3)+}\end{matrix}\right\}\rightleftarrows \left\{\begin{matrix}MY^{(m-4)+}\\ \uparrow\downarrow\\ MHY^{(m-3)+}\end{matrix}\right\}+\left\{\begin{matrix}M'^{m'+}\\ \uparrow\downarrow\\ M'(OAc)_{n'}^{(m'-n')+}\end{matrix}\right\} \quad (2)$$

In this paper are presented the formation constants of acetatocadmium(II) and acetatocobalt(II) complexes which have been determined by the same procedure as used for the acetato complexes of copper(II), lead(II) and zinc(II).

Experimental

Reagent.—Standard solutions of copper(II) nitrate and cadmium(II) nitrate were prepared by dissolving known amounts of pure copper and pure cadmium metals (Merck Co. Ltd.), respectively, in reagent-grade nitric acid. In the case of cadmium metal, the oxide layer on the metal surface was removed with hydrochloric acid. This cadmium metal was found by the a. c. polarographic method to contain 0.08% of lead as impurity. The careful examination, however, showed that this minute quantity of lead would give no appreciable effect on the equilibrium determination, and therefore no further purification was carried out. The solution of disodium ethylenediaminetetraacetate (EDTA) was standardized against the standard solution of copper(II) nitrate by amperometric titration with the dropping mercury electrode[3]. A standard solution of cobalt(II) nitrate was prepared by dissolving an appropriate

1) N. Tanaka and K. Kato, This Bulletin, **32**, 516 (1959).
2) N. Tanaka and K. Kato, ibid., **33**, 417 (1960).
3) N. Tanaka, M. Kodama, M. Sasaki and M. Sugino, *Japan Analyst* (*Bunseki Kagaku*), **6**, 86 (1957).

amount of cobalt metal in reagent-grade nitric acid. Its concentration was determined with the standardized EDTA solution volumetrically using murexide as an indicator[4] and also amperometrically using the dropping mercury electrode as an indicator electrode[3]. The polarographic analysis showed that the cobalt metal contained 0.2% of nickel as impurity. Therefore, the equilibrium study of the reaction involving cobalt(II) ions or cobalt(II)-EDTA complexes was carried out, taking into consideration the substitution reaction involving nickel(II)-EDTA complexes (see below).

Sodium acetate-acetic acid buffers were prepared by mixing the solutions of sodium carbonate and acetic acid. Sodium carbonate, acetic acid and other reagents used for the supporting electrolyte were of guaranteed reagent grade and used without further purification.

Apparatus and procedure. — A Shimadzu RP-2 pen-recording polarograph and a manual apparatus similar to that of Kolthoff and Lingane[5] were used for the measurement of current-voltage curves. Two dropping mercury electrodes were used. One had an m value of 2.57 mg./sec. and a drop time τ of 3.52 sec. in an air-free acetate buffer of pH 4.7 containing 0.1 M acetate, 0.1 M potassium nitrate and 0.01% gelatin at 25°C with open circuit. The other had an m value of 2.93 mg./sec. and a drop time τ of 3.16 sec. in an air-free 0.1 M potassium nitrate solution at 25°C with open circuit. A saturated calomel electrode with a large area was used as the anode, which was connected to the electrolytic solution by a Hume and Harris-type agar bridge[6]. A Hitachi Model EHP-l pH meter was used for the pH measurement. Dissolved oxygen in the solution was removed by bubbling pure tank nitrogen through the solution.

The measurements of the diffusion current of copper(II) in acetate buffer solutions were carried out with the following two reaction mixtures:

(a) copper(II)—cadmium(II)—EDTA

(b) copper(II)—cobalt(II)—EDTA.

The measurements were made at 15, 25 and 35°C in acetate buffers of pH 4.75 (for cadmium(II)) and pH 4.70 (for cobalt(II)) of which the acetate concentrations were varied from 0.02 M to 0.10 M (for cobalt(II)) or to 0.15 M (for cadmium(II)). The ionic strength was adjusted to be 0.2 with potassium nitrate. Gelatin was added as a maximum suppressor by 0.01% in concentration.

In the preliminary experiments, it was found that the substitution reactions between copper(II) ions and cadmium(II)-EDTA complexes and those between copper(II) ions and cobalt(II)-EDTA complexes proceeded at considerable reaction rates. The reaction mixtures of the copper(II)-cadmium(II)-EDTA system were kept standing at the given temperature for ten to twenty hours after the preparation and were subjected to the measurement, though they were found to reach nearly the equilibrium within 60 minutes. In the case of the copper(II)-cobalt(II)-EDTA system, the diffusion currents of the copper(II) in the reaction mixtures were measured 45 min. after the preparation at 15°C, 30 min. at 25°C and 25 min. at 35°C. This was decided from the consideration of the effect of the reaction between copper(II) and nickel(II)-EDTA complexes on the equilibrium under consideration, because the cobalt(II) solution used in this experiment contained a small amount of nickel as impurity. It was found in the preliminary experiments that the reaction between copper(II) and nickel(II)-EDTA complexes affect more or less the equilibrium concentration of copper(II) in the substitution reaction between copper(II) and cobalt(II)-EDTA complexes after the above-mentioned period, though the former reaction proceeds at much slower rate than the latter[7].

Results

The apparent diffusion current constants[2] of copper(II) were determined by measuring the diffusion current at various acetate concentrations. The values of $[Cu^{2+}]_{app}$ which is given by[2]

$$[Cu^{2+}]_{app} = [Cu^{2+}] + \sum_{1}^{n} [Cu(OAc)_n^{(2-n)+}] \tag{3}$$

were determined with the aid of those apparent diffusion current constants from the diffusion currents obtained with the reaction mixtures of systems a and b. Then, the apparent equilibrium constants ($K^{M}_{M',app}$) for Eq. 2, expressed as[2]

$$K^{M}_{M',app} = \frac{[M'^{m'+}]_{app}\{[MY^{(m-4)+}] + [MHY^{(m-3)+}]\}}{[M^{m+}]_{app}\{[M'Y^{(m'-4)+}] + [M'HY^{(m'-3)+}]\}} \tag{4}$$

were culculated. The F_n functions expressed as[2]

$$F_0 \equiv K^{M}_{M',app}\left\{1 + \sum_{1}^{n} K_{M(OAc)}[OAc^-]^n\right\} = K^{M}_{M'}\frac{\beta}{\beta'}\left\{1 + \sum_{1}^{n'} K_{M'(OAc)_{n'}}[OAc^-]^{n'}\right\} \tag{5}$$

$$F_1 = \frac{F_0 - \frac{\beta}{\beta'}K^{M}_{M'}}{\frac{\beta}{\beta'}K^{M}_{M'}[OAc^-]} = K_{M'OAc} + K_{M'(OAc)_2}[OAc^-] + \cdots\cdots \tag{6}$$

$$F_2 \equiv \frac{F_1 - K_{M'OAc}}{[OAc^-]} = K_{M'(OAc)_2} + K_{M'(OAc)_3}[OAc^-] + \cdots\cdots \tag{7}$$

.....

4) G. Schwarzenbach, "Complexometric Titrations" translated by H. Irving, Methuen & Co. Ltd., London (1957), p. 78.

5) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, Interscience Publishers, New York (1952), p. 297.

6) D. N. Hume and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **15**, 465 (1943).

7) unpublished work.

$$F_{n'} \equiv \frac{F_{n'-1} - K_{M'(OAc)_{n'-1}}}{[OAc^-]} = K_{M'(OAc)_{n'}} \quad (8)$$

were successively obtained, where $K^{M}_{M'}$ means the true equilibrium constant given by

$$K^{M}_{M'} = \frac{[M'^{m'+}]\,[MY^{(m-4)+}]}{[M^{m+}]\,[M'Y^{(m'-4)+}]} \quad (9)$$

and β and β' are

$$\beta = 1 + K^{H}_{MHY}[H^+]$$

$$\beta' = 1 + K^{H}_{M'HY}[H^+]$$

The results obtained for systems a and b are given below. The values of β/β' were calculated to be approximately unity for both a and b systems at the pH's in the present experiments, using the equilibrium constants K^{H}_{MHY} and $K^{H}_{M'HY}$ given by Schwarzenbach, Gut and Anderegg[8].

(a) Copper(II)–Cadmium(II)–EDTA System. —The formation constants of acetatocadmium (II) complexes were determined by the measurement of $K^{Cu}_{Cd,app}$ at various acetate concentrations with the aid of the formation constants of $CuOAc^+$ and $Cu(OAc)_2$ obtained in the previous paper[2], where, under the experimental condition, $K^{Cu}_{Cd,app}$ is given by the equation

$$K^{Cu}_{Cd,app} = \frac{[Cd^{2+}]_{app}\{[CuY^{2-}] + [CuHY^-]\}}{[Cu^{2+}]_{app}\{[CdY^{2-}] + [CdHY^-]\}}$$

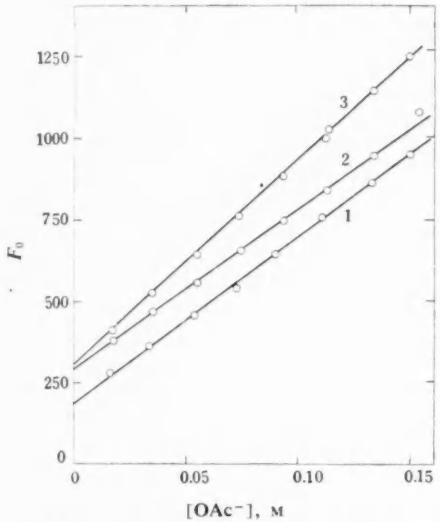

Fig. 1. F_0 (Eq. 5) as a function of the acetate ion concentration in copper(II)–cadmium(II)–EDTA system: 1, at 15°C; 2, at 25°C; 3, at 35°C.

8) G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954).

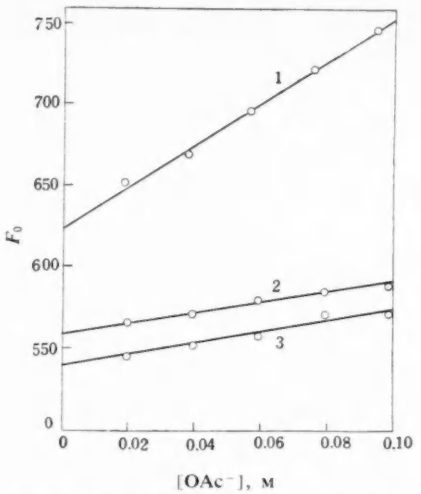

Fig. 2. F_0 (Eq. 5) as a function of the acetate ion concentration in copper(II)–cobalt(II)–EDTA system: 1, at 15°C; 2, at 25°C; 3, at 35°C.

The values of F_0 given by Eq. 5 were calculated and plotted against the acetate ion concentration. These plots for 15, 25 and 35°C are shown in Fig. 1, in which all F_0 plots give straight lines indicating that at acetate concentrations up to 0.15 M $CdOAc^+$ is only species of acetatocadmium(II) complex which exists in the solution at an appreciable concentration. The formation constants of $CdOAc^+$ are listed in Table I.

(b) Copper(II)–Cobalt(II)–EDTA System. —The formation constants of acetatocobalt(II) complexes were determined with the same procedure as for the acetatocadmium(II) complexes. $K^{Cu}_{Co,app}$ which is given by the equation

$$K^{Cu}_{Co,app} = \frac{[Co^{2+}]_{app}\{[CuY^{2-}] + [CuHY^-]\}}{[Cu^{2+}]_{app}\{[CoY^{2-}] + [CoHY^-]\}}$$

was determined at various acetate concentrations. In this case also, the F_0 plots gave straight lines as shown in Fig. 2. From these plots the formation constants of $CoOAc^+$ were determined, which are given in Table I.

Table I. Formation constants of acetatocadmium(II) and acetatocobalt(II) complexes at various temperatures

Metal ions	Temp., °C	K_{MOAc} (μ=0.2)
Cadmium(II)	15	27
	25	16
	35	20
Cobalt(II)	15	2.1
	25	0.6
	35	0.6

TABLE II. SOME EXAMPLES OF THE REPORTED VALUES OF FORMATION CONSTANTS OF ACETATOCADMIUM(II) AND ACETATOCOBALT(II) COMPLEXES

Metal ion	Investigator	Method	Temp., °C	Ionic strength	K_{MOAc}	$K_{M(OAc)_2}$	Ref.
Cadmium(II)	I. Leden et al.	Potentiometric	25	3	20	190	9, 10
	A. Jacques	〃	25	≃0.5	100	~150	11
	E. Ferrell et al.	〃	20	≦0.55	50	—	9, 12
Cobalt(II)	S. Bardhan et al.	Potentiometric	35	0	23	—	13
				0.2	7.6*		(13)
	S. K. Siddhanta et al.	〃	30~35	0	33	127	14
				0.2	11*	22*	(14)

* Those values are the formation constants which were calculated by the present authors with the values reported in the literature referred to. In the calculation, the activity coefficients of cadmium(II), cobalt(II) and acetate ions were estimated to be 0.30, 0.33 and 0.73, respectively, and the activity coefficient of monoacetato complexes was assumed to be equal to that of acetate ions[2,15].

Discussion

The formatiom constants of the acetato complexes of cadmium(II) and cobalt(II) have been reported by several researchers. In Table II some of them are given, which are compared with the formation constants listed in Table I.

Recently, Yasuda and Yamasaki[16] determined the formation constants of acetato complexes of some bivalent metal ions and found that the stabilities of those complexes decreased in the order of $Pb > Cu > Cd > Zn > Ni$. The formation constants of K_{MOAc} obtained in the previous[1,2] and present investigations agree with the above order.

The equilibria of the substitution reaction represented by Eq. 1 have been studied with the same procedure as that reported previously[2]. The equilibrium constants, K_{Cd}^{Cu} and K_{Co}^{Cu}, are given in Table III. Schwarzenbach and his co-workers[8] studied the substitution reaction of copper(II) ions and cadmium(II)-EDTA complexes at 20°C in the solution of ionic strength 0.1 with 8×10^{-3} M sodium acetate. The equilibrium constant which was reported by those researchers was corrected for the acetato complex formation using the formation constants K_{CuOAc}, $K_{Cu(OAc)_2}$ and K_{CdOAc}. The resulting constant is also given in Table III. On the other hand, no investigation had been reported on the substitution reaction between copper(II) ions and cobalt(II)-EDTA complexes. Therefore, the equilibrium constant of the reaction was calculated with the formation constants of copper(II)-EDTA and cobalt(II)-EDTA complexes[8]. This is also shown in Table III. It is seen that the K_M^M values obtained in this study are in satisfactory agreement with those calculated from the equilibrium or the formation constants reported by Schwarzenbach et al.

TABLE III. EQUILIBRIUM CONSTANTS FOR THE SUBSTITUTION REACTION (EQ. 1) AT IONIC STRENGTH 0.2 COMPARED WITH SCHWARZENBACH'S VALUES

Temp., °C	$K_{Cd}^{Cu}\times10^{-2}$		$K_{Co}^{Cu}\times10^{-2}$	
	I	II	I	III
15	1.9	—	6.2	—
20	—	2.6±0.5	—	4.4±2.0
25	3.0	—	5.6	—
35	3.1	—	5.4	—

I. Values obtained in the present investigation.
II. Values calcuated from the Schwarzenbach's $K_{Cd,\,app}^{Cu}$[8].
III. Values calculated from the formation constants[8].

Summary

The formation constants of acetatocadmium-(II) and acetatocobalt(II) complexes were determined at ionic strength of 0.2 at 15, 25 and 35°C with the procedure that is based on the polarographic measurement of the sum of the equilibrium concentrations of the hydrated metal ions and the metal acetate complexes in the substitution reaction involving EDTA complexes. The resulting formation constants K_{CdOAc} and K_{CoOAc} are 27 and 2.1 at 15°C, 16 and 0.6 at 25°C and 20 and 0.6 at 35°C, respectively.

9) J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants of Metal Ion Complexes, Part I, Organic Ligands," the Chemical Society, London (1957), Special Publ. No. 6, p. 3.
10) I. Leden, *Svensk Kem. Tidskr.*, **58**, 129 (1946); Doctoral Diss., Lund, 1943, 89.
11) A. Jacques, *Trans. Faraday Soc.*, **5**, 225 (1910).
12) E. Ferrell, J. M. Ridgion and H. L. Riley, *J. Chem. Soc.*, **1934**, 1440.
13) S. Bardhan and S. Aditya, *J. Indian. Chem. Soc.*, **32**, 109 (1955).
14) S. K. Siddhanta and S. N. Banerjee, *Ibid.*, **35**, 343 (1958).
15) J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).
16) M. Yasuda and K. Yamasaki, presented at the Symposium on Metal Complexes, Fukuoka, October, 1959.

The authors thank the Ministry of Education for the financial support granted for this research.

Department of Chemistry
Faculty of Science
Tohoku University
Katahira-cho, Sendai

Infrared Spectrum of Some Deuterated Crystalline Polystyrenes. I. Isotactic Poly-αd_1-styrene

By Masamichi KOBAYASHI

(Received April 14, 1960)

During these a few years many studies have been made on the molecular structure of the stereospecific vinyl polymer, and it has been found that most of isotactic polymers have the helical structure in their crystalline regions mainly because of steric hindrances of side groups.

To make clear the helical structure of the polymer molecule, infrared spectroscopy is one of the most powerful methods as well as X-ray analysis.

Recently, Tadokoro et al[1]. reported the studies on the infrared spectra of isotactic polystyrene and its α, β, β-tri-deuterated derivative and detected that in the spectrum of the polystyrene the absorption bands appearing in region of 1400~1180 cm^{-1}, such as the bands at 1364, 1314, 1297 and 1185 cm^{-1}, are characteristic of the three-fold helical structure of the polystyrene molecule and assumed to be associated with the vibrations of CH_2, CH and the carbon skeletal chain.

To make the assignments of these bands more clearly it is desirable to study the spectra of several other deuterated derivatives. For this purpose, isotactic poly-αd_1-styrene was prepared and its infrared spectrum was studied.

Experimental

1. Preparation of αd_1-Styrene.—αd_1-Styrene was prepared by hydrolysis with deuterium oxide of the Grignard reagent of α-bromostyrene. From the massspectroscopic data, it was proved that the monomer prepared contained 99.5% of d_1-styrene. The infrared spectrum of this monomer is shown in Fig. 1 (solid line) in comparison with that of styrene (dotted line). It is justifiable to regard the sample as αd_1-styrene from a few spectroscopic evidences; the appearance of the band at 2230 cm^{-1} corresponding to the stretching vibration of CD group, the shift of the band corresponding to the C=C stretching from 1628 to 1614 cm^{-1} on deuteration and appearances of the bands corresponding to the bending vibration (at near 1400 cm^{-1}) and the rocking vibration (at near 1160 cm^{-1}) of CH_2 group in the spectra of both monomers.

To determine more precisely the position of the

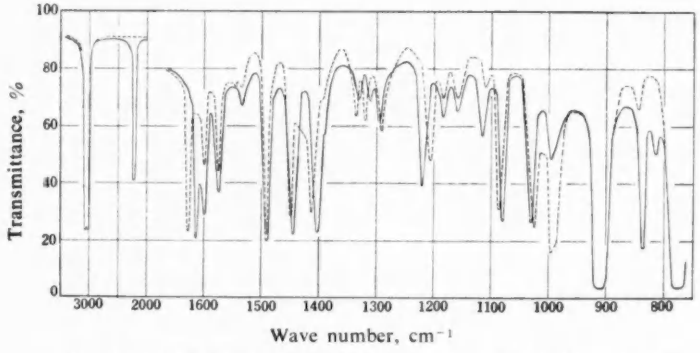

Fig. 1. Infrared spectra of αd_1-styrene (——) and styrene (——).

1) H. Tadokoro, N. Nishiyama, S. Nozakura and S. Murahashi, *J. Polymer Sci.*, **36**, 553 (1959).

deuterium atom in this monomer, the proton magnetic resonance spectrum of this monomer was compared with that of styrene. The spectra were measured using a Nihon Denshi Kogaku N. M. R. spectrometer.

Proton signals of the spectrum of styrene, from lower to higher field, are assigned[2] to H_1, H_2, H_4 and H_3 respectively as shown in Fig. 2. While the signals due to H_3 and H_4 of styrene both split into quartets by spin coupling with H_2 and with each other, the spectrum of the ethylenic protons of the deuterated styrene is doublet with some closely spaced fine structure. If a small coupling constant between H_3 and H_4 is taken into account, this deuterated styrene can be identified as αd_1-styrene.

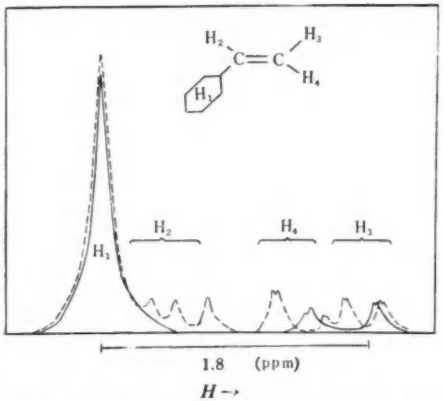

Fig. 2. Proton magnetic resonance spectra of αd_1-styrene (——) and styrene (----) at 40 Mc/sec.

2. Polymerization and Preparation of the Samples for I. R. Measurements.—The monomer was polymerized with Ziegler catalyst ($AlEt_3+TiCl_4$) in *n*-heptane and the polymer prepared was purified by the usual method. The films cast from the toluene solution were oriented by drawing them to about five times their original lengths in boiling water and were crystallized by heating at 60°C for 10 minutes in glycerol.

The I. R. spectra were measured in the region of 3500~400 cm^{-1} using a Hilger H800 I. R. spectrometer and the polarized spectra were measured in the region of 3500~650 cm^{-1} using a selenium polarizer.

Experimental Results

In Fig. 3a and 3b are shown the polarized spectra of isotactic poly-αd_1-styrene in the region of 3500~2000 cm^{-1} and 1600~650 cm^{-1} respectively. The wave numbers, the dichroisms and the relative intensities of the absorption bands are given in Table I in comparison with those of isotactic polystyrene.

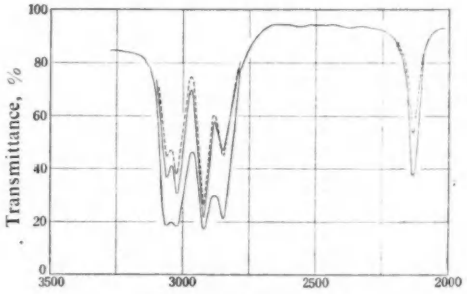

Fig. 3a. Infrared dichroisms of isotactic poly-αd_1-styrene.
—— electric vector perpendicular to elongation
---- electric vector parallel to elongation

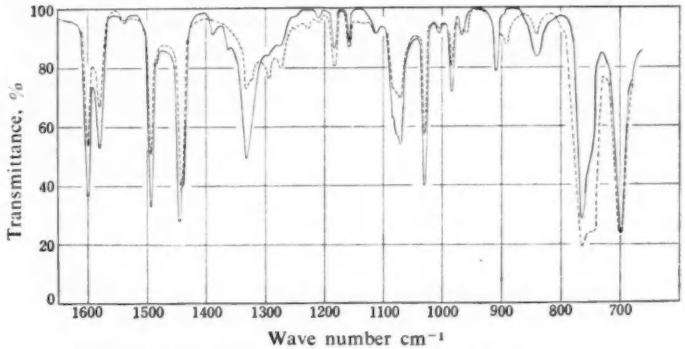

Fig. 3b. Infrared dichroisms isotactic poly-αd_1-styrene.
—— electric vector perpendicular to elongation
---- electric vector parallel to elongation

2) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance", McGraw-Hill Book Company, Inc., New York (1959), p. 238.

TABLE I. INFRARED SPECTRA OF ISOTACTIC POLYSTYRENE AND ISOTACTIC POLY-αd_1-STYRENE AND VIBRATIONAL ASSIGNMENTS

Polystyrene			Poly-α d_1-styrene			Assignments
Freq. (cm^{-1})	Dichr.	R. I.	Freq. (cm^{-1})	Dichr.	R. I.	
3082	σ	mw	3082	σ	mw	
3060	σ	s	3060	σ	s	ν(CH) phenyl
3025	σ	s	3025	σ	s	
2923	σ	vs	2923	σ	vs	$\nu(CH_2)$ asym
2849	—	s	2849	—	s	$\nu(CH_2)$ sym.
			2134	σ	m	ν(CD)
1602	σ	s	1600	σ	s	k* mode A_1
1580	σ	ms	1580	σ	ms	l* mode B_1
1493	σ	s	1495	σ	s	m* mode A_1
1452	σ	vs	1447	σ	vs	n* mode B_1
1444	—	ssh	1440	—	ssh	$\delta(CH_2)$ A−E
1389	σ	vw	1388	σ	vw	
1364	σ	ms				δ(CH)E
			1334	σ	ms	δ(CD)E ?
1314	σ	m				
1297	π	mw	1295	π	mw	w(CH_2)A
			1275	π	w	δ(CD)
1261	σ	w				
			1227	π	vw	
			1210	σ	vw	
1195	π	mw				w(CH)A
1185	π	mw	1183	π	mw	ν(CC)A
1180	?	mw	(1180)**			δ(CH) phenyl
1154	—	mw	1158	—	mw	c* mode B_1
1110	σ	w	1115	σ	w	
1080	σ	m	1084	σ	m	CH (or CD), CH_2+
			1072	σ	msh	phenyl
1048	σ	m				
1028	σ	ms	1031	σ	ms	b* mode A_1
1005	σ	w	1005	σ	w	p* mode A_1
985	σ	m	985	σ	m	cryst. sensitive
964	—	w	968	—	w	h* mode A_2
			960	π	w	w(CD)A
920	σ	m				
906	π	m	910	—	m	i* mode B_2
898	π	mw	891	π	mw	
842	σ	mw	842	σ	w	g* mode A_2
783	π	ssh				
755	π	vs	765	π	vs	f* mode B_2
			748	π	ssh	
			705	π	vs	
700	π	vs	700	π	vs	
615		w	615		w	s* mode B_1
579		mw	570		mwsh	skeletal
557		s	557		s	v* mode+skeletal
489		vw	489		vw	skeletal

* Assignments of the normal mode of monosubstituted benzene according to Whiffen's notation.
** This band is assumed to overlap the band at 1183 cm^{-1}.

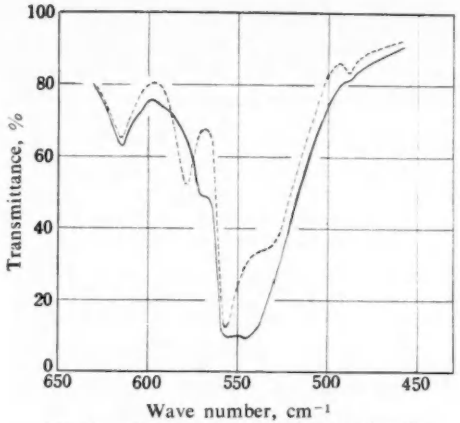

Fig. 3c. Infrared spectra of isotactic poly-αd_1-styrene (——) and isotactic polystyrene (----).

Discussions

1. General Discussions.—In the crystalline region, the molecule of isotactic polymer consists of a sequence of repeating units with a regular spatial arrangement. Strictly speaking, therefore, the molecular vibrations of the whole polymer molecule should be considered for the analysis of the absorption bands. Nevertheless, the normal modes of the phenyl group and the skeletal chain may be analyzed separately for the sake of simplicity. Comparing the spectrum of the isotactic polystyrene with that of the atactic one, most of the absorption bands associated with the phenyl group differ from each other by a small amount and, hence, this approximation seems reasonable for our case.

Since the molecular vibrations of the phenyl groups of polystyrene and its deuterated derivatives in which the deuterium is substituted in the skeletal chain may be regarded as those of monosubstituted benzene having a point symmetry C_{2v}[3], the assignments of some bands of these polymers immediately can be made from the well-known results on the molecular vibrations of monosubstituted benzene. In our case, the assignments are made according to Whiffen's notaion[4]. The results are given in the last column of Table I. These bands are common to polystrene and the deutero-derivatives in wave number and dichroism. The bands assignable to the modes belonging to A_1 species, e. g., 1600, 1495, 1031 cm^{-1} bands, and B_1 species, e. g., 1580, 1462 cm^{-1} bands have σ nature, and, on the other hand, B_2 species, e. g., 765 cm^{-1} band, have π nature. These polarization properties may be interpreted by the molecular structure determined by Natta and Corradini[5].

The σ band which is crystallization-sensitive appears at the same wave number, 985 cm^{-1}, as those of polystyrene and poly-α, β, β d_3-styrene. This may be due to interactions between the phenyl groups of the neighboring molecules in the crystalline lattice.

In Fig. 3c are shown the spectra of isotactic poly-αd_1-styrene (solid line) and isotactic polystyrene (dotted line) in the region of 650~450 cm^{-1}. The band at 557 cm^{-1} which has been detected[6] as characteristic of the isotactic configuration of the polystyrene molecule also appears in isotactic poly-αd_1-styrene. This band might be assigned to the v-mode coupling with the skeletal vibration.

The molecular vibrations of the skeletal chain (consisting of CH (or CD) and CH_2 groups) of isotactic polystyrene or isotactic poly-αd_1-styrene may be considered as those of a one-dimensional three-fold helical chain having a point symmetry C $(2\pi/3)$[7]. From the factor group analysis it is concluded that the normal vibrations of this chain are divided into two symmetry species; A (non-degenerate) and E (doubly degenerate), and the fundamentals of the former should have π nature and those of the latter σ nature. In physical meanings, the symmetry species correspond to the phase differences between the vibrations of the neighboring monomer units. Therefore, the normal modes of the helix can be considered as ones composed of the basic modes of the monomer units.

As for the stretching vibrations of CH_2 and CH (or CD) groups and the CH_2 bending vibration, the normal modes under the symmetry species A have almost the same frequencies as those under E species. The observed absorption band due to each of such modes, therefore, may be considered as that consisting of two overlapping bands, one being assigned to the mode under A and another to that under E.

The polarization properties of these bands depend on the chain conformation of the polymer molecule. In the spectrum of poly-αd_1-styrene, the band at 2923 cm^{-1} (antisymmetric CH_2 stretching) has σ nature and the band at 2849 cm^{-1} (symmetric CH_2 stretching)

3) C. Y. Liang and S. Krimm, *J. Polymer Sci.*, **27**, 241 (1958).
4) D. C. Whiffen, *J. Chem. Soc.* **1956**, 1350.
5) G. Natta and P. Corradini, *Makromol. Chem.*, **16**, 77 (1955).
6) M. Kobayashi, presented at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1959.
7) C. Y. Liang and S. Krim, *J. Chem. Phys.*, **25**, 563 (1956).

shows almost no dichroism. These results coincide whih Tadokoro et al.'s results on isotactic polystyrene and its several derivatives[8]. The band at 2134 cm^{-1} (CD stretching) has σ nature, and the band at 1440 cm^{-1} (CH_2 bending) shows almost no dichroism. Dichroic ratio is expressed for a uniaxial orientation as

$$(A_{\parallel}/A_{\perp}) = 2\cot^2\psi$$

where ψ is the angle between the transition moment accompanied with the vibration and the fiber axis.

The dichroic ratios calculated on the basis of the predicted molecular conformation are as follows; zero for $\nu_{asym}(CH_2)$, 0.78 for $\nu_{sym}(CH_2)$ and $\delta(CH_2)$, and 0.27 for ν(CD). The results well fit the polarization properties of these bands.

As for the deformation vibrations of CH_2 and CH (or CD) groups except $\delta(CH_2)$, the frequencies of the normal modes under A species, in general, differ from those under E. Since the relative intensity of each fundamental of these modes depends on the chain conformation of the polymer molecule, the assignments of some bands, therefore, may be made from the polarization properties and the relative intensities of the bands. Further, the changes in spectrum on deuteration give us some additional information for this purpose. On the basis of the molecular structure of isotactic polystyrene, it seems reasonable that relatively large intensities are expected for the banbs assignable to the deformation of CH (or CD) under E, δ(CH)E (δ(CD)E), the wagging of CH (or CD) under A, w(CH)A (w(CD)A), the rocking of CH_2 under E, r(CH_2)E, the wagging of CH_2 under A, w(CH_2)A, and the stretching of the skeletal carbon atoms under A, ν(CC)A.

2. Bands in the Region of 1400~1180 cm^{-1}. —In this region appear the bands which have been considered by Tadokoro et al. as characteristic to the helical structure of polystrene.

The σ band at 1364 cm^{-1} of isotactic polystyrene disappears on deuteration, and the corresponding σ band of similar intensity appears at 1334 cm^{-1} in poly-αd_1-styrene. This fact may support the assumption that the band at 1364 cm^{-1} is mainly due to δ(CH)E. Whether the 1334 cm^{-1} band may be assigned to δ(CD)E is still in question, for there is a possibility of the appearance of the band associated with the phenyl group at this position.

The 1297 cm^{-1} band of isotactic polystyrene appears also in isotactic poly-αd_1-styrene, but not in the trideutero-derivative. Therefore, this band may be assigned to w(CH_2)A.

In the spectrum of isotactic polystyrene, there are three bands, i. e., 1195 (π), 1185 (π) and 1180 cm^{-1} (?) bands in the vicinity of 1180 cm^{-1}. The two π bands disappear in isotactic poly-αd_1-styrene. Since the CC stretching band and the CH wagging band are expected to be observed in this region, it seems reasonable to presume that one of them is due to ν(CC)A and another is to w(CH)A. The following facts may be cited to support the assignments of ν(CC)A to the 1185 cm^{-1} band and w(CH)A to the 1195 cm^{-1} band. (1) The 1195 cm^{-1} band appears in isotactic poly-βd_1-styrene.[9] (2) The 1183 cm^{-1} band of poly-αd_1-styrene shows a remarkable π nature. Although a band assignable to the a-mode (A_1) of the phenyl group is expected to appear in the vicinity of 1180 cm^{-1}, the 1183 cm^{-1} band could not be assigned to this mode because of its polarization property. Therefore, this may be due to the overlapping of the CC stretching mode and the a-mode.

The weak π band appears at 1275 cm^{-1} on deuteration. This may be due to the CD deformation. The weak π band at 960 cm^{-1} which appears on deuteration may be assigned to w(CD)A.

3. Other Bands. —Remarkable changes in the spectrum on deuteration are observed in the regions of 1085~1040 cm^{-1} and 920~810 cm^{-1}. While the atactic polystyrene band at 1070 cm^{-1} splits into two σ bands at 1080 and 1048 cm^{-1}, the corresponding bands of isotactic poly-αd_1-styrene appear at 1084 cm^{-1} and 1072 cm^{-1}. It seems reasonable to assume these bands as associated rather with the characteristics of the helical polymer chain themselves than with the interaction between the neighboring molecules in the crystalline lattice, for these bands do not disappear even at molten state. From the fact that the bands corresponding to them do not appear in some ring-substituted derivatives, e. g., poly-*p*-deutero-styrene[8] or poly-*p*-halogeno-styrenes[10], these may be due to the coupling of a vibrational mode of the phenyl group and that of CH_2 or CH (or CD).

Corresponding to the bands of isotactic polystyrene at 920 (σ), 910 (no dichroism) and 898 (π) cm^{-1} which are very sensitive to the crystallization degree of the sample, the π band and the band showing almost no dichroism appear at 891 cm^{-1} and 910 cm^{-1}

8) H. Tadokoro, S. Nozakura, T. Kitazawa, Y. Yasuhara and S. Murahashi, This Bulletin, **32**, 313 (1951); S. Murahashi, S. Nozakura and H. Tadokoro, ibid., **32**, 534 (1959).

9) M. Kobayashi, presented at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1960.

10) K. Nagai, M. Kobayashi and E. Nagai, presented at the 8th Annual Meeting of the Society of Polymer Science of Japan, Tokyo, May, 1959.

respectively in isotactic poly-αd_1-styrene. The band at near 910 cm^{-1} of both polymers may be assigned to an out-of-plane deformation of CH of the phenyl group (probably i-mode) since the corresponding band appears also in poly-α, β, βd_2-styrene. The assignments of the other two bands are left uncertain for the present.

Summary

In Table I are given the results of discussions described above on the assignments of the absorption bands.

The bands characteristic to the isotactic polymers, i. e. the bands appearing in the region of 1400~1180 cm^{-1} or in the vicinity of 1070 and 900 cm^{-1}, are proved as associated with the CH_2 and CH groups.

To make assignments of the bands more precisely, the studies are in progress on the infrared spectra of the other several deuterated derivatives, such as poly-βd_1-, poly-α, βd_2 and poly-β, β d_2-styrenes.

The author is indebted to Mr. Seiichi Mima for mass spectroscopic measurements and to Mr. Hiroshi Shima for measurements of proton magnetic resonance spectra.

Osaka Industrial Research Institute
Oyodo-ku, Osaka

On the Infrared Spectra of Crystalline Poly-p-fluorostyrene

By Masamichi KOBAYASHI, Kazuo NAGAI and Eiichi NAGAI*

(Received April 30, 1960)

During the last few years, many isotactic vinyl polymers have been obtained from various ring-substituted styrene monomers with Ziegler type catalysts[1]. Most of them crystallize with helical molecular conformation similar to that of isotactic polystyrene, but the pitches of the helixes are different from each other depending on the size, the site and the number of substituents. For instances, while poly-*o*-fluorostyrene crystallizes in three-fold helix with the identity period of 6.65 Å, but poly-*p*-fluorostyrene in four-fold helix with the period of approximately 8.3 Å[1]. Further, it has been noticed by Murahashi et al.[2] that the polymers of *p*-methyl, *m*-methyl and *p*-trimethylsilyl styrene prepared with Ziegler catalyst have larger fiber periods of 12.9, 57 and 60.4 Å, respectively.

Recently, from the infrared spectroscopic studies on several isotactic polymers, Tadokoro et al.[3] found that the characteristics of helical structure of the polymers would be indicated in common by the infrared dichroisms of the several absorption bands, especially of the stretching vibrations of the CH_2 groups. Keeping in mind their findings, we measured the infrared spectra of crystalline poly-*p*-fluorostyrene with an aim to find in what respects they would reflect the characteristics of the helical structure of its own.

As a result, it was found that the dichroic ratios of the bands, especially those assigned to the stretching vibrations of CH_2 groups differed from those of polystyrene.

To obtain a theoretical ground for this fact, we calculated the dichroic ratios of the bands associated with CH_2 and CH groups, assuming the polymer chain to have a four-fold helical structure allowed for the observed fiber period.

On the other hand, we analyzed the infrared spectrum of the polymer under the assumption that they, in an approximation, may be divided into two parts, one being associated with the side group and another with the skeletal chain. The molecular vibrations of the former were analyzed in terms of D_{2h} symmetry and those of the latter in terms of $C(\pi/2)$ symmetry.

Experimental

p-Fluorostyrene (4 g.) prepared by an usual method was polymerized in *n*-heptane at 70°C for 10 hr. using triethyl aluminum (0.53 g.) + titanium tetrachloride (0.18 g.) as a catalyst in a sealed tube. The solid product was washed with hot methanol and then boiled in water to change the organometallic compounds contaminated in the polymer into insoluble oxides. The white polymeric substance was dissolved in boiling xylene and the

* Present address: Takatsuki Laboratory, Kureha Boseki Co. Ltd., Takatsuki, Osaka.

1) G. Natta, F. Danusso and D. Sianesi, *Makromol. Chem.*, **28**, 253 (1958).

2) S. Murahashi, S. Nozakura, and H. Tadokoro, This Bulletin, **32**, 534 (1959).

3) H. Tadokoro, S. Nozakura, T. Kitazawa, Y. Yasuhara and S. Murahashi, This Bulletin, **32**, 313 (1959).

solution was filtered. The gelatinous precipitate separated from the filterate kept at room temperature was dried after centrifugation.

To gain a high degree of crystallinity, the polymer film cast from the toluene solution was subjected to heat-treatment at 160°C for 1 hr. in glycerol. It had the density of 1.23 and melting point of 240°C. The oriented film for measurements of the polarized spectrum was made by drawing it to five times the length of the original in boiling water.

The infrared measurements were made in the region of 3500~400 cm^{-1} using Hilger H 800 and Perkin Elmer Model 21 I. R. spectrometers; the former was equipped with the polarizer consisting of a set of six selenium films, each approximetely 5 μ. thick. The amorphous polymer for comparison was prepared with benzoyl peroxide as a catalyst.

Experimental Results

X-ray Diagram. — In Fig. 1 is illustrated the X-ray fiber diagram of the stretched film of crystalline poly-*p*-fluorostyrene (abbreviated to PFS). The measured identity period along the fiber axis was 8.31 Å being similar value reported by Natta et al.[1] This value assumes that the polymer chain is of isotactic configuration and takes four-fold helix in the crystalline regions. The calculated angles

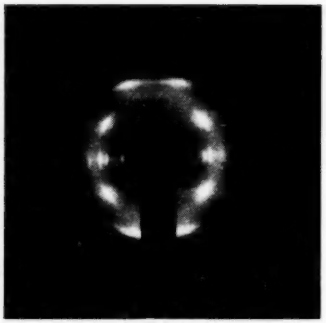

Fig. 1.

of internal rotation of the chain about the C–C bonds with which the helix is formed will be presented later.

Infrared Spectra.—In Fig. 2 are shown the spectra infrared in the region of 3500~400 cm^{-1} of atactic and isotactic PFS together with that of the latter measured at molten state.

In Fig. 3 are shown the polarized spectra of isotactic PFS in the region of 3500~650 cm^{-1}.

The wave numbers, the dichroisms and the relative intensities of the absorption bands are given in Table I.

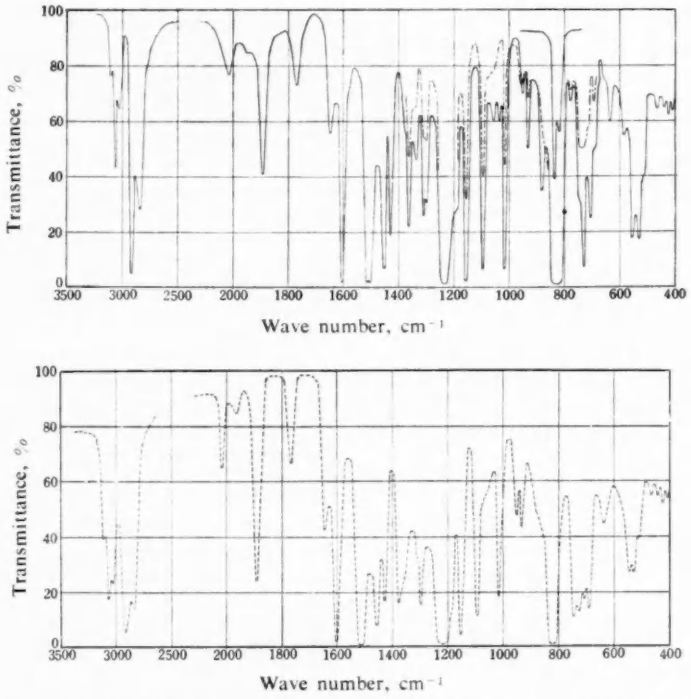

Fig. 2. Infrared spectra of PFS; isotactic at crystalline state ——, isotactic at molten state — —, atactic ----.

TABLE I. BAND ASSIGNMENTS OF THE SPECTRA OF ISOTACTIC AND ATACTIC PFS

Isotactic cryst.			Isotactic molt.		Atactic		Assignment
Freq. (cm^{-1})	Dichr.	R. I.	Freq. (cm^{-1})	R. I.	Freq. (cm^{-1})	R. I.	
3112	σ	vw	3112	vw	3112	vw	A_g+B_{2g}
3060	σ	m	3060	m	3060	m	B_{3u}
3026	σ	w	3026	w	3026	w	B_{1u}
2924	σ	s	2924	s	2924	s	ν_{asym} (CH_2)
2849	π	m	2849	m	2849	m	ν_{sym} (CH_2)
2047	σ	w	2047	w	2047	w	530+1515=2045
1891	σ	m	1891	m	1891	m	819+1096=1915
1770	σ	w	1770	w	1770	w	
1647	σ	w	1647	w	1647	w	B_{3u}
1603	—	s	1603	s	1603	s	A_g
1515	σ	s	1515	s	1515	s	B_{1u}
1503	—	s					
1454	(σ)	s	1454	s	1457	s	δ (CH_2)
1448	(π)	s	1448	s	1448	s	
1428	σ	ms	1428	ms	1428	ms	
1377	—	sh	1377	sh	1377	m	
1361	σ	m	1361	m			δ (CH)E
1336	π	w	1336	sh			
1309	σ	m	1309	m	1309	sh	
1300	π	m	1300	m	1300	m	w (CH_2)A
1234	—	vs	1234	vs	1234	vs	ν $(CF)A_g$
1191	π	sh	1191	sh			ν (CC)A
1154	σ	s	1154	s	1154	s	ν $(CF)B_{1u}$
1096	σ	s	1096	s	1096	s	B_{3u}
1056	σ	w	1056	sh	1056	sh	B_{3u}
1035	σ	w					
1015	σ	s	1015	s	1015	s	B_{1u}
950	—	w	950	w	950	w	A_u
932	—	m	932	w	932	w	B_{3g}
881	σ	m	881	sh	881	sh	
832	—	vs	832	vs	832	vs	B_{2u}
819	π	vs	819	vs	819	vs	A_g
738	—	sh	738	sh	748	s	
730	—	s	725	s	725	ms	B_{1u}
708	σ	m	708	sh	708	mw	r (CH_2)E ?
694	σ	s	694	w	694	m	
634		w	634	w	634	w	δ $(CF)B_{2g}$
583		msh	583	msh			
555		s	553	s	545	s	
530		s	530	s	530	s	δ $(CF)B_{2u}$
515		wsh	515	sh	515	sh	
464		vw	464	vw	464	vw	A_g
444		vw	444	vw	444	vw	
425		vw	425	vw	425	vw	δ $(CF)B_{3u}$
410		vw	410	vw	410	vw	

Discussions

In this paper the molecular vibractions of the polymer molecule with four-fold helical structure are analyzed following the same way as described in the previous paper[4] on isotactic poly-αd_1-styrene; the vibrations of the side group and the skeletal chain are considered separately.

Vibrational Modes of the Side Group. — The molecular vibrations of the side group of PFS correspond to those of *p*-disubstituted benzene. The data useful for our study have

4) M. Kobayashi, to be published in this Bulletin.

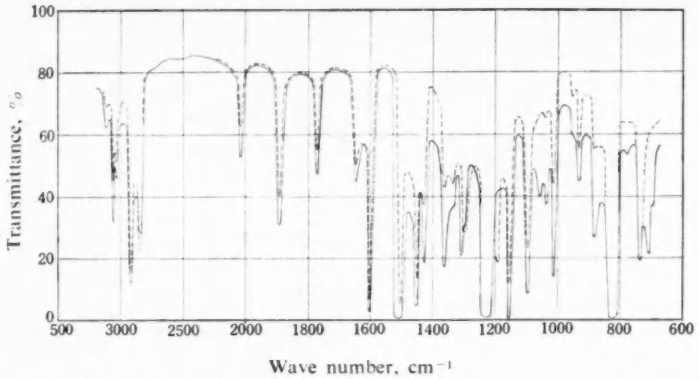

Fig. 3. Infrared dichroism of isotactic PFS. —— Electric vector perpendicular to elongation. ---- Electric vector parallel to elongation.

TABLE II. CHARACTER TABLE, NUMBER OF NORMAL MODES AND SELECTION RULES FOR POINT GROUP D_{2h}

	E	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	i	$C_2(z)$	$C_2(y)$	$C_2(x)$	Zero fr.	n	Selec. rule
A_g	+1	+1	+1	+1	+1	+1	+1	+1		6	R.
A_u	+1	−1	−1	−1	−1	+1	+1	+1		2	—
B_{1g}	+1	+1	−1	−1	+1	+1	−1	−1	R_z	1	R.
B_{1u}	+1	−1	+1	+1	−1	+1	−1	−1	T_z	5	I.R.
B_{2g}	+1	−1	+1	−1	+1	−1	+1	−1	R_y	5	R.
B_{2u}	+1	+1	−1	+1	−1	−1	+1	−1	T_y	3	I.R.
B_{3g}	+1	−1	−1	+1	+1	−1	−1	+1	R_x	3	R.
B_{3u}	+1	+1	+1	−1	−1	−1	−1	+1	T_x	5	I.R.

already been published. Freguson et al.[5] and Tobin[6] have made assignments of the absorption bands of *p*-fluorotoluene and *p*-dichlorobenzene respectively. In applying their results to our aim, it is assumed that the analysis using a point group of D_{2h} woluld be preferable, if it is taken into account that fluorine atom and CH group attached to the para position of benzene nucleus are similar in mass.

Symmetry species, irreducible representations, numbers of normal modes and selection rules for the point group D_{2h} are given in Table II. The selection rules can not be applied rigorously in our case, since the two substituents at the para positions will not suffer the same transition moment. As a result, the fundamentals under all species would become Raman active and those except A_u and B_{1g} infrared active. Referring to the assignments of the bands of *p*-fluorotoluene given by Freguson, we selected out from the spectrum of PFS the bands which might be assigned to the vibrational modes of the side group. They are given in Table III.

It is, of course, anticipated that they will be more or less under the influences of the crystalline field. In fact, considerable differences are observed in some of the bands before and after crystallization or on melting. For example, the band at 1056 cm^{-1} assigned to CH in-plane deformation (B_{3u}) becomes sharper and the intensity of the band at 932 cm^{-1} assigned to CH out-of-plane deformation (B_{3g}) increases on crystallization.

Vibrations of the Skeletal Chain. — Since the molecule of isotactic PFS has four-fold helical structure in the crystalline region, the molecular vibrations of the skeletal chain may be accounted for by using the factor group $C(\pi/2)$[7]. From the result of the factor group analysis, the normal modes are divided into three symmetry species; A (non-degenerate), B (non-degenerate) and E (doubly degenerate) species. Symmetry species, irreducible representations, selection rules and numbers of the normal modes are given in Table IV. In the calculation of the numbers of the normal modes, the side group attached to the skeletal chain is taken as a mass point. The modes under A and E are infrared active and ones under B are inactive. The fundamentals under

5) E. E. Freguson, R. L. Hudson, J. Rud Nielsen and D. C. Smith, *J. Chem. Phys.*, 21, 1736 (1953).
6) M. C. Tobin, *J. Phys. Chem.*, **61**, 1392 (1957).
7) C. Y. Liang and S. Krimm, *J. Chem. Phys.*, **25**, 563 (1956).

TABLE III. ASSIGNMENTS OF THE BANDS DUE TO THE SIDE GROUP

p-FT	PFS		*p*-FT	PFS	
ν (CH)			δ $(C\text{-}C\text{-}C)_{in}$		
3071	3112	A_g	1099	1096	B_{3u}
3071	3112	B_{2g}	728	730	B_{1u}
3069	3060	B_{3u}	455	464	A_g
3043	3026	B_{1u}	313		B_{2g}
δ (CH)			ring		
1222	(1211)	B_{2g}	842		A_g
1044	1056	B_{3u}			
1017	1015	B_{1u}	δ $(C\text{-}C\text{-}C)_{out}$		
825	819	A_g	695	694	B_{3g}
			390		A_u
γ (CH)			152		B_{2u}
956	950	A_u			
929	932	B_{3g}	ν (CF)		
817	832	B_{2u}	1214	1234	A_g
(810)		B_{1g}	1157	1154	B_{1u}
ν (CC)			δ (CF)		
1614	1647	B_{3u}	638	634	B_{2g}
1602	1603	A_g	503	530	B_{2u}
1512	1515	B_{1u}	422	425	B_{3u}
1299	(1300)*	B_{2g}	341		B_{3g}

ν (CH); CH stretching, δ (CH); CH in-plane deformation, γ (CH); CH out-of-plane deformation, ν(CC); CC stretching, δ $(C\text{-}C\text{-}C)_{in}$; CC in-plane deformation, δ $(C\text{-}C\text{-}C)_{out}$; CC out-of-plane deformation, ν (CF); CF stretching, δ (CF); CF deformation.

* The 1300 cm^{-1} band observed may be due mainly to w (CH_2).

A and E should exhibit parallel (π) and perpendicular (σ) dichroisms respectively. Physically, the symmetry species A, E and B mean that the neighboring monomer units constituting the helix vibrate with a definite phase difference of 0, $\pm\pi/2$ and π, respectively.

Infrared Dichroism. — Bearing in mind the fact noted in the introduction that infrared dichroisms of several bands, especially of those due to the CH_2 stretching vibrations, have been detected as reflecting helical structures of the isotactic polymers, the infrared dichroisms of the stretched film of isotactic PFS were measured (see Fig. 3). It was demonstrated that the 2849 cm^{-1} band assigned to the CH_2 symmetric stretching exhibited a considerable π nature and the 2924 cm^{-1} band assignable to the CH_2 antisymmetric stretching showed a slight σ nature. These facts do not coincide with Tadokoro et al.'s results on isotactic polystyrene and others; the former band shows almost no dichroism and the latter a considerable σ nature.

This discrepancy may be attributed to the reason that the plane of the methylene group in the helix of PFS is inclined to the fiber axis in a different way from that of isotactic polystyrene. In other words, this is attributed to the difference in conformation of the skeletal carbon chain between them.

To gain a concrete ground for this, we calculated the theoretical dichroic ratios ($A_{\parallel}/A_{\perp}$) of the absorption bands. In doing this, however, precise knowledge about the conformation of the molecule of PFS is needed. For this purpose, the data available at present is the observed fiber period of the polymer. A helical structure of an isotactic polymer which gives a definite identity period is determined by the angles of internal rotation of the chain elements about the C–C bonds, provided that the length of C–C bond and the bond angle are kept at constant.

From the mathematical calculations presented in the appendix, we can search for the angles of internal rotation which will fulfill the conditions that the helix of PFS has the observed identity period of 8.31 Å and contains four monomer units in one pitch. In Table V is given the relation between the angles of internal rotation (θ_1 and θ_2) and the calculated identity period, R. In this table ν_x, ν_y and ν_z are the components of the unit vector of the fiber axis in an internal Cartesian coordinate. Using them, calculation of the dichroic ratio may be made.

θ_1 (or θ_2) is the angle with which a given bond is rotated from the trans position with the clockwise direction taken as plus when seen from the lower indexed carbon atom (see Fig. 4). If $\theta_1=0°$ and $\theta_2=120°$, R will give an identity period 6.65 Å of the three-fold helix (isotactic polystyrene).

The most reasonable values of θ_1 and θ_2 for PFS will be present between $-10°$ and $-12°$ and between 94° and 95° respectively, provided

TABLE IV. SYMMETRY SPECIES, IRREDUCIBLE REPRESENTATIONS, NUMBER OF NORMAL MODES AND SELECTION RULES FOR POINT GROUP $C(\pi/2)$

	E	C^1	C^2	C^3	N	Zero fr.	n	I.R.	R.
A	+1	+1	+1	+1	18	T_z, R_z	16	A	A
B	+1	−1	+1	−1	18		18	F	A
E	+1	+i	−1	−i	18	(T_σ, R_σ)	(16)	A	A
	+1	−i	−1	+i	18			A	A

TABLE V. ANGLES OF INTERNAL ROTATION AND FIBER PERIOD FOR FOUR-FOLD HELIX

θ_1	θ_2	ν_x	ν_y	ν_z	$R^{*,**}$
0	90	0.438	0.899	0	8.86 Å
−10	94	0.368	0.926	−0.081	8.39
−12	95	0.354	0.930	−0.098	8.29

* Assuming C–C bond length of 1.54 Å and C–C–C bond angle of 116°.
** The observed fiber period of PFS is 8.31 Å.

that the C–C–C bond angle takes the same value as that of polystyrene, 116°.

Dichroic ratio is expressed for a uniaxial orientation as follows;

$$A_{\parallel}/A_{\perp}=2\cot^2\varphi$$

where φ is the angle between the transition moment and the fiber axis. If a unit vector $\boldsymbol{m}$ of a transition moment accompanied with a vibrational mode of the CH_2 group is defined by the components m_x, m_y and m_z in the Cartesian system (x_1, y_1, z_1), it follows that

$$\cos\varphi=\boldsymbol{\nu}^{\top}\cdot\boldsymbol{m}=\nu_x m_x+\nu_y m_y+\nu_z m_z$$

On the other hand, if a unit vector $\boldsymbol{m}'$ of a transition moment accompanied with a vibrational mode of the CH or the phenyl group is defined by the components m'_x, m'_y and m'_z in the Cartesian coordinate (x_{1+i}, y_{1+i}, z_{1+i}), the corresponding expression is

$$\begin{aligned}\cos\varphi&=\boldsymbol{\nu}^{\top}\cdot\boldsymbol{A}_1\boldsymbol{m}'\\&=\nu_x(m'_x\cos\omega+m'_y\sin\omega)\\&+\nu_y(m'_x\sin\omega\cos\theta_1\\&-m'_y\cos\omega\cos\theta_1+m'_z\sin\theta_1)\\&+\nu_z(m'_x\sin\omega\sin\theta_1\\&-m'_y\cos\omega\sin\theta_1+m'_z\cos\theta_1)\end{aligned}$$

where $\boldsymbol{A}_1$ is the matrix of the orthogonal transformation defined in the appendix.

Using the values of ν_x, ν_y and ν_z, the dichroic ratios of the absorption bands due to the vibrational modes of the CH_2 and CH groups were calculated. The results are given in Table VI.

It is shown as expected that they depend on the angles of internal rotation, θ_1 and θ_2. The changes in dichroic ratio of the bands due to the CH_2 stretching vibrations are of importance by reason of that described above. The dichroic ratios of the ν_{sym} (CH_2) band and the ν_{asym} (CH_2) band increase with θ_2.

TABLE VI. THE CALCULATED DICHROIC RATIOS FOR FOUR-FOLD HELICAL POLYMER

Vibrational mode	$\theta_1=0°$	$\theta_1=-10°$	$\theta_1=-12°$
ν_{sym} (CH_2), $\bar{\sigma}$ (CH_2)	0.781	1.073	1.132
ν_{asym} (CH_2), r (CH_2)	0	0.013	0.019
w (CH_2)	5.122	3.626	3.422
$\bar{\sigma}$ (CH)	0	0.013	0.019
w (CH)	5.122	3.626	3.422

Since when $\theta_1=0$, the calculated values do not depend on the number of monomer unit in one pitch provided that the bond angle is kept at constant ($\theta_2=120°$ for three-fold helix, $\theta_2=90°$ for four-fold helix), the values for $\theta_1=0°$ may be regarded as those of isotactic polystyrene. Therefore, the results well explain the differences between PFS and polystyrene in polarization property of the bands due to the CH_2 stretching vibrations.

Although the coincidence between the observed property and the predicted value of dichroism of the ν_{asym} (CH_2) is yet qualitative, it would be accepted as correct if we take into account of the contribution from the chain segments randomly oriented in the amorphous regions.

Absorption Bands Characteristic to the Helical Structure of PFS. —As in the cases of polystyrene and its several derivatives, the bands characteristic of the helical structure (alternate sequence of trans and gauche conformations) of the polymer molecule are observed in the spectrum of isotactic PFS. They do not disappear even at molten state and are assumed to be associated mainly with the deformational vibrations of the CH_2 or CH group or the skeletal modes.

The band at near 1450 cm^{-1} may be ascribed to the CH_2 bending ($\bar{\sigma}(CH_2)$). Using the differential method it was made clear that this band consisted of two bands at 1454 and 1448 cm^{-1}, having σ and π nature respectively, and the former might be assigned to $\bar{\sigma}(CH_2)E$ and the latter to $\bar{\sigma}(CH_2)A$.

The five bands at 1361 (σ), 1336 (π), 1309 (σ), 1300 (π) and 1191 (π)cm^{-1} of isotactic PFS may correspond to the bands which have been detected by Tadokoro et al. as characteristic of the helical structure of isotactic polystyrene and others. Measurements of the dependence of the spectrum on temperature showed that with increasing temperature the band at 1336 cm^{-1} decreased its relative intensity and disappeared at molten state, on the other hand, the other four bands were hardly affected by temperature change. Then, the four bands may be considered as indicating rather the characteristics of the polymer molecule itself than the interactions of neighboring molecules in the crystalline lattice.

On the basis of the results on the assignments of the bands characteristic of isotactic polystyrene[1], the assignments of these bands may be made as follows; the 1361 cm^{-1} band is assigned to the CH deformation under the E species ($\bar{\sigma}$ (CH)E), the 1300 cm^{-1} band to the CH_2 wagging under the A species (w

$(CH_2)A$), the 1191 cm^{-1} band to the CC stretching under the A species (ν (CC)A). The 1309 cm^{-1} band is still unassigned.

The difference between isotactic PFS and atactic one in spectrum are observed also in the region of 690~750 cm^{-1}. The band at 738 cm^{-1} of isotactic PFS has smaller intensity than the corresponding band at 748 cm^{-1} of atactic one. This fact remains even at molten state. The σ band at 708 cm^{-1} of isotactic PFS decreases its intensity with increasing temperature, on the other hand, the band at 694 cm^{-1} shows the reverse change. Although the CH_2 rocking mode is anticipated to be ovserved in this region and, from polarization property, the 708 cm^{-1} bond is assumed to be assigned to it, the precise assignment to date is open to question.

The results of the discussions on the assignments of the absorption bands are given in the last column of Table I.

Appendix

The Geometrical Structures of Polymers with Helical Structure. — Spatial configuration of a vinyl polymer is determined primarily by angles of internal rotation of C–C bonds. If the spatial position of each monomer unit in the helix is equivalent, the conformation of the polymer chain is defined by two angles of internal rotation as described below. The internal Cartesian coordinates are defined as shown in Fig. 4. The matrix which transforms the coordinate from $(x_{i+1}, y_{i+1}, z_{i+1})$ to (x_i, y_i, z_i) system, or from $(x_{i+2}, y_{i+2}, z_{i+2})$ to $(x_{i+1}, y_{i+1}, z_{i+1})$ system is represented by $\boldsymbol{A}_1$ (or $\boldsymbol{A}_2$);

$$\boldsymbol{A}=\begin{pmatrix}\cos\omega & \sin\omega & 0\\ \sin\omega\cos\theta & -\cos\omega\cos\theta & \sin\theta\\ \sin\omega\sin\theta & -\cos\omega\sin\theta & -\cos\theta\end{pmatrix}$$

where $\theta=\theta_1(\boldsymbol{A}_1)$ or $\theta=\theta_2(\boldsymbol{A}_2)$, and ω is the supplement angle of C–C–C and angle.

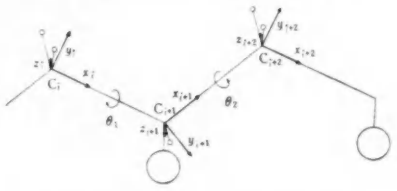

Fig. 4. Internal coordinates for vinyl polymer.

If the unit vector of the fiber axis in (x_i, y_i, z_i) system is defined by $\boldsymbol{\nu}$ $(\nu_x, \nu_y, \nu_z)^\top$, the following relation is introduced;

$$\boldsymbol{\nu} = \boldsymbol{A}_1\boldsymbol{A}_2\boldsymbol{\nu}$$

Since $\boldsymbol{A}$'s are matrixes of orthogonal transformation,

$$(\boldsymbol{A}_1{}^\top-\boldsymbol{A}_2)\boldsymbol{\nu}=\boldsymbol{0}$$

Then, it follows that

$$(\cos\theta_1-1)\nu_y+(\sin\theta_1)\nu_z=0 \quad (1)$$

$$\sin\omega(1-\cos\theta_2)\nu_x+\cos\omega(\cos\theta_2-\cos\theta_1)\nu_y -(\cos\omega\sin\theta_1+\sin\theta_2)\nu_z=0 \quad (2)$$

$$-(\sin\omega\sin\theta_2)\nu_x+(\sin\theta_1+\cos\omega\sin\theta_2)\nu_y +(\cos\theta_2-\cos\theta_1)\nu_z=0 \quad (3)$$

As $\boldsymbol{\nu}$ is unit vector

$$\nu_x{}^2+\nu_y{}^2+\nu_z{}^2=1 \quad (4)$$

If the fiber period of n-fold helix is $\boldsymbol{R}$,

$$\boldsymbol{R}/n=\boldsymbol{\nu}^\top\cdot(\boldsymbol{b}+\boldsymbol{A}_1\boldsymbol{b})$$

where

$$\boldsymbol{b}=(b,\ 0,\ 0)^\top$$

b is the CC bond length. Therefore,

$$R/n=b\{(1+\cos\omega)\nu_x+(\sin\omega\cos\theta_1)\nu_y +(\sin\omega\sin\theta_1)\nu_z\} \quad (5)$$

To construct n-fold helix, the following condition must be satisfied; the angle between the projection of $\overline{C_iC_{i+1}}$ to the plane perpendicular to the fiber axis and the one of $\overline{C_{i+2}C_{i+3}}$ to the same plane must be $2\pi/n$. Then,

$$(\boldsymbol{A}_1\boldsymbol{A}_2\boldsymbol{1}\times\boldsymbol{\nu})\cdot(\boldsymbol{1}\times\boldsymbol{\nu})=\cos(\pi-2\pi/n)$$

Then,

$$\cos^2\omega+\sin^2\omega\cos\theta_2 -\{\nu_x{}^2+\nu_x\nu_y\sin\omega\sin\theta_1\sin\theta_2 -\nu_x\nu_z(1+\cos\theta_1)\sin\omega\sin\theta_2\} =\cos(n-2)\pi/n \quad (6)$$

Provided that fiber period, C–C–C bond angle, C–C bond length and number of monomer units in one pitch of the helix are known, it is possible to calculate the angles of internal rotation, θ_1 and θ_2, using the Eqs. 1—6.

In Table V are given the results of the calculation for four-fold helix. In this calculation, the C–C bond length of 1.54 Å and the C–C–C bond angle of 116° are assumed.

Osaka Industrial Research Institute
Oyodo-ku, Osaka

Neutron Activation Analysis of Halogens in High-Purity Silicon

By Tadashi NOZAKI, Toshi KAWASHIMA, Hideo BABA and Hidemaro ARAKI

(Received May 6, 1960)

Extreme purification is of vital importance when silicon is used as a semiconductor material, and many papers treating many kinds of trace impurity in high-purity silicon have been published. However, neither the method of the determination nor the behavior of halogens in a given material has been studied enough. Previously, we reported[1] on the neutron activation analysis of iodine in silicon. In this paper, a method for simultaneous determination of chlorine, bromine and iodine in one sample is presented with some results.

Fusion of the neutron-irradiated silicon with potassium hydroxide containing potassium iodide as carrier was proved suitable for decomposing the sample in the determination of iodine. A similar fusion with alkali chloride, bromide and iodide as carrier should serve satisfactorily for their simultaneous determination. On such fusion under a reducing atmosphere, both chlorine and bromine in the sample will be converted into chloride and bromide respectively. Even if they were present in other forms than halide ions, they would be converted into chloride and bromide, when the basic cake is dissolved in an aqueous sulfuric acid in the presence of a large excess of iodide. Although perchlorate is not readily reduced to chloride on such a treatment, the formation of perchlorate under the given condition is least probable. Thus the carriers should work satisfactorily.

When a sulfuric acid solution containing the three halides was distilled in the presence of chromium(VI) oxide, the following three fractions of the distillate were successively obtained: (1) light brown solution containing bromine, (2) almost colorless solution containing only a small amount of halogen, (3) faintly yellow solution containing chlorine and hydrogen chloride. Addition of a sufficient quantity of oxalic acid and some water into the residual solution resulted in the reduction of the iodate to iodine. This was easily distilled, purified and converted into silver iodide for β-ray counting.

The bromine must be carefully purified. This is because after neutron irradiation of natural bromine, three radioactive nuclides of bromine are present as shown in Table I. The radiochemical purity of the bromine sample, however, can be checked precisely neither from its decay curve nor from the γ-ray spectrum. The first fraction, containing some chlorine and perhaps a trace of iodine too, was submitted, before being converted into silver bromide for counting, to a further purification, whose usefulness was checked by a tracer technique using ^{36}Cl and ^{131}I. On the

TABLE I. RADIOACTIVE NUCLIDES OF THE HALOGENS FORMED BY THE NEUTRON IRRADIATION

Nuclide	Half-life	β-Ray energy (MeV.)	γ-Ray energy (MeV.)	*Activity formed (dpm)
^{36}Cl	3×10^{5}y	β^-0.704 (98%)	none	negligible
^{38}Cl	37.3m	β^-4.81 (53%) 2.77 (16%) 1.11 (31%)	2.15 (31+16%) 1.60 (31%)	5.4×10^{10}
^{80m}Br	4.4h		0.049 0.037	5×10^{10}
^{80}Br	17.6m	β^-1.99 (72%) etc. β^+0.87 (3%)	0.62 (13%)	1.1×10^{12}
^{82}Br	35.9h	β^-0.444 (100%)	0.55, 1.47 eight γ-rays	9×10^{7}
^{128}I	25.0m	β^-2.12 (76%) etc.	0.46 (17%) others (weak)	8×10^{11}

* Just after 1 hr's irradiation of 1 g. of a natural halogen under a thermal neutron flux of 6×10^{11} n/cm^2 sec.

1) T. Nozaki et al., This Bulletin, 33, 320 (1960).

other hand, chlorine in the third fraction was converted into silver chloride for counting without further purification, for it involves some difficulty and is time-consuming, and there is no possible nuclide that enters the silver chloride and decays with a similar half-life emitting an energetic γ-ray. The silver chloride was proved to be radiochemically pure, as far as the distillation was carried out with care to prevent contamination with radioactive silica.

When the sample contains by far the least amount of iodine amidst the three halogens, there is another preferable process, which consists of the distillation of iodine after the treatment of the fused cake as reported previously and the separation of bromine and chlorine by the method indicated above. The two complete processes require nearly equal time, with a good yield and radiochemical purity.

Unfortunately, fluorine can not be determined by a similar technique because of the lack of a suitable radioactive nuclide formed by neutron irradiation.

Experimental

Sample.—All of the silicon samples were of transistor grade, purified by the chloride process (in U. S. A.), by the iodide process (in the Electrical Communication Laboratory) or by an unknown method (in Europe). Many other impurities in them were determined by emission spectroscopy or by neutron activation analysis with an irradiation under a higher flux and for a longer period, the results indicating their high purity. In most cases, two portions of the same sample were analyzed, each being 0.5 to 1 g.

Irradiation.—The samples enveloped in thick polyethylene sheets were irradiated in a water boiler type reactor, (Japan Research Reactor 1) for an hour under a neutron flux of about $6\times10^{11}\,n/cm^2$ sec., placed side by side with the radioactivation standard of ammonium chloride, ammonium bromide and potassium iodide, and taken out swiftly through a neumatic tube.

Chemical Separation.—The irradiated samples were etched with a mixture of hydrofluoric and nitric acid, to avoid possible surface contamination pulverized, weighed and fused with potassium hydroxide (10 to 15 g.) kept just above its melting point and containing a known ammount of sodium chloride, potassium bromide and potassium iodide (each 5 to 10 mg.) as carriers. The fused cake was dissolved in sulfuric acid (2 : 3, 100 ml.) containing a small quantity of sodium sulfite (about 0.01g.). The solution was transferred into a crooked neck distillation flask (in order to protect the distillate from contamination by the radioactive silicon) and distilled after the addition of chromium(VI) oxide (10 g.).

The bromine distilled out in the first few minutes. The colored distillate was caught in an aqueous sodium sulfite (25 ml. of 10 g./l. solution) containing sodium chloride and potassium iodide (each a few mg.), oxidized by adding concentrated phosphoric acid (10 ml.) and potassium permanganate (20 ml. of 10 g./l. solution), and the bromine was extracted with carbon tetrachloride (20 ml.), back-extracted with hydroxylamine (0.1 g.) in nitric acid (1 : 100, 20 ml.) and converted into silver bromide.

A tracer study to prove the usefulness of this purification was carried out preliminarily by the use of ^{36}Cl and ^{131}I. On oxidation with permanganate, no detectable ^{36}Cl (less than 1/5,000) entered the organic phase, but a trace of iodine did when the treatment was performed with less care. However, the iodine was removed completely (to less than 1/5,000) by back-extraction, for a solution of hydroxylamine in dilute nitric acid reduces molecular bromine to bromide and oxidizes iodide to iodine.

The distillation was continued, and after several minutes from the disappearence of the bromine color when a faint color of chlorine became recognizable by a careful observation, the distillate was introduced into an aqueous sodium sulfite (10 g./l. 25 ml.). When the color of chlorine in the distillate disappeared, the chloride was converted into silver chloride without further purification. It was somewhat preferable to carry out the distillation of bromine with a smaller amount (1 g.) of chromium(VI) oxide and to add a larger amount (10 g.) before the distillation of chlorine.

When the determination of iodine was necessary, it was attained by adding a sufficient quantity (more than 30 g.) of oxalic acid and some water (30 ml.) into the residual solution, distilling the liberated iodine and converting it into silver iodide after the purification as mentioned previously[1].

Each silver halide was filtered off with a glass filter (No. 3), washed with nitric acid (1 : 100, 50 ml.), water, ethanol and ether, and submitted to counting and weighing. The time required for the chemical process was less than an hour for bromine, about one hour for chlorine and 1.2 hr. for iodine, with a yield exceeding 50%.

Radioactivation Standard.—Each of the irradiated bromide and iodide was dissolved in water containing a known amount of the same halide as carrier, and converted into silver bromide and iodide after being purified by the oxidation, extraction and back-extraction. On the other hand, silver chloride was precipitated without purification.

Counting.—A simple G-M counter of an end window type was used in all cases. For chlorine, a scintillation counter with a large sodium iodide crystal (4″×4″) and a single channel analyzer was also used (the region between 1.8 MeV. and 3.5 MeV.). More precise determination could be done by the latter, but the efficiency of the former was somewhat higher. The decay curve of the chlorine measured by a G-M counter agreed well with that of the standard sample and the theoretical curve. The agreement of the decay curve of the bromine and iodine with that of the corresponding standard was complete. For lowering the detection limit, use of a 2π counter was also examined, and its efficiency was found to be about five times higher

than that of the G-M counter with the sample kept as near as possible.

Results and Discussion

Some of the results are shown in Tables II and III. It is natural that a silicon purified by the chloride method contains a trace of chlorine and that purified by the iodide method contains iodine. On the other hand, it should be an interesting fact that most of the high-purity silicons contain two other halogens too, indicating a tendency that the less the concentration of a halogen becomes, the greater the persistency with which it remains in the silicon. Silicon powder obtained by the thermal decomposition of silicon tetraiodide usually contained several ppm of iodine. The iodine content could be lowered down to about 0.3 ppm by a simple technique (i.e. fusion under an argon flow or segregation). Table III indicates the segregation of iodine in a single crystal of silicon about 7 cm. long prepared by pulling it from the melt at a rate of 1 cm. per min. Here, it is also shown tha the iodine content decreased fairly rapidly down to 0.3 to 0.2 ppm. However, a high-purity silicon prepared by the iodide process and purified by 30 times' zone refining still contained nearly the same amount of iodine. On the other hand, a determination showed that heating in a hydrogen atmosphere seems to be effective to reduce the iodine as low as several hundredths ppm.

TABLE II. HALOGEN CONTENT OF HIGH-PURITY SILICONS

Method of purification	Halogen content (ppm)		
	Cl	Br	I
Chloride method	2.2	0.18	0.15
Iodide method	0.2	0.05	0.38
(Unknown)	<0.15	<0.02	0.17

TABLE III. SEGREGATION OF IODINE

Location (centimeter from the tail)	0.3	1.6	2.9	4.8	6.2
Iodine content (ppm)	1.5	0.94	0.83	0.32	0.22

As the result, a trace of any of the three halogens remains in a high-purity silicon quite persistently after many physical purifications, and the persistency increases with the decrease of its concentration. The authors are wishing to elucidate this reason.

When it is assumed that an activity of 150 cpm at the initiation of counting is essential for precise identification of the nuclide, the detection limit is 1.5×10^{-7} g., 1.5×10^{-8} g. and 3.0×10^{-8} g. for chlorine, bromine and iodine respectively by the use of a G-M counter and under the conditions described above. Use of a 2π counter could lower the limit down to one-fifth of the above values.

Summary

A trace quantity of chlorine, bromine and iodine was determined simultaneously by neutron activation analysis. By careful distillation of a solution containing the alkali-fused silicon, chromium(VI) oxide and sulfuric acid, bromine and chlorine were distilled out separately, leaving iodine in the residual solution, which was then distilled out after adding oxalic acid.

Most kinds of high-purity silicon contained more than 0.1 ppm of a halogen, which was used in the course of its purification process, and also two other halogens, though of a smaller quantity.

The authors acknowledge with thanks the help given by the Staff Members of the Japan Atomic Energy Research Institute.

The Electrical Communication Laboratory
Musashino, Tokyo

Long-chain Phosphates. I. Reactions of Solid Potassium Kurrol Salt with Solutions of Various Metal Salts

By Shigeru OHASHI and Kazuo YAMAGISHI

(Received May 12, 1960)

Long-chain potassium metaphosphate, $(KPO_3)_n$, which is called potassium Kurrol salt, can be readily prepared by dehydrating potassium dihydrogen orthophosphate. It is a well-known fact[1] that potassium Kurrol salt is not easily soluble in pure water, but dissolution takes place in dilute solutions of salts of alkali metals other than potassium to give a highly viscous solution which is characteristic of a linear polymer of a high molecular weight. Thilo et al.[2,3], investigated the reactions between solutions of potassium Kurrol salt and those of various metal ions. It is the purpose of this paper to present some information on the behavior of potassium Kurrol salt in a solid state toward solutions of various metal ions. Solid potassium Kurrol salt reacts with solutions of certain multivalent cations to give gummy substances. The authors investigated particularly in details a reaction of potassium Kurrol salt with nickel ion, since the colored substance produced allowed easy observation upon the process of the reaction. The results indicated that the potassium ion in solid potassium Kurrol salt can be replaced by the nickel ion in a solution through a cation-exchange process. In the course of this investigation Weiss and Michel[4] found that reactions of solid potassium Kurrol salt with solutions of various alkylammonium ions can be regarded as a cation-exchange process.

Experimental

Preparation of Potassium Kurrol Salt.—Potassium Kurrol salt is usually prepared by dehydrating potassium dihydrogen orthophosphate. Pfanstiel and Iler[5] investigated the effect of minute variations in the original K/P ratio on the viscosity of the solution of potassium Kurrol salt and indicated that when there is a deficiency of potassium in a starting material, cross-linking occurs between phosphate polymer chains in the resulting potassium Kurrol salt crystal. An excess of potassium in a starting material forms potassium tripolyphosphate as a separate phase. Pfanstiel and Iler[5] gave the relationship between pH of a 0.1 M solution of potassium dihydrogen orthophosphate and its K/P ratio.

A 0.1M solution of potassium dihydrogen orthophosphate of Wako special grade (lot 1335) was prepared in carbon dioxide-free distilled water. The pH of the solution was 4.50. According to Pfanstiel and Iler's data the K/P ratio of the potassium dihydrogen orthophosphate was calculated to be 0.9998 ± 0.0008. This value means that no further adjustment of the K/P ratio is necessary for the present purpose.

In a platinum dish 156.4 g. of the potassium dihydrogen orthophosphate was dehydrated at a lower temperature than the melting point, 807°C, of potassium Kurrol salt. Then it was melted in an electric furnace at 870°C. After being kept at this temperature for 30 min., it was gradually cooled to 775°C in 3 hr. After being kept at 775°C for 25 hr., the sample was removed from the furnace and chilled by holding the lower part of the dish in water. A transparent crystalline product was prepared. According to Malmgren and Lamm's study[6,7] the molecular weight of the potassium Kurrol salt prepared in this work was presumed to be about 10^6.

X-ray Diffractometry.— X-ray patterns of the potassium Kurrol salt as well as hydrated metaphosphate containing potassium and nickel and its dehydrated products were taken with Copper K_α radiation and a nickel filter by means of an automatic recording X-ray diffractometer, "Geigerflex", of Rigaku Denki Co., Ltd. For the potassium Kurrol salt a rotating mount was used to avoid the preferred Crientation.

Paper Chromatography.—Two-dimensional paper chromatography was carried out according to Karl-Kroupa's procedure[8]. Acid solvent was made by mixing 735 ml. of isopropyl alcohol, a solution of 50 g. of trichloroacetic acid in 265 ml. of water, and 2.5 ml. of concentrated aqueous ammonia. Basic solvent was made by mixing 387 ml. of isopropyl alcohol, 200 ml. of isobutyl alcohol, 408 ml. of water, and 5 ml. of concentrated aqueous ammonia. Filter papers used in this work were Toyo No. 53.

Analytical Methods for the Determination of Phosphate, Potassium, Nickel and Other Metal Ions.—For the determenation of phosphate, potassium, and nickel ions in a solid and an aqueous

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6) H. Malmgren and O. Lamm, *Z. anorg. allgem. Chem.*, **252**, 256 (1944).
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8) E. Karl-Kroupa, *Anal. Chem.*, **28**, 1091 (1956) and her private publication.

phase obtained by the reaction of the potassium Kurrol salt with an aqueous solution of nickel sulfate, the following method was used. An aliquot of the solution was charged into an ion-exchange column of Dowex 1-X4 of chloride form and the column was washed with water. From the solution which passed through the column, the nickel ion was precipitated with dimethylglyoxime and aqueous ammonia and determined gravimetrically. After the separation of nickel the filtrate containing the potassium ion was evaporated to dryness in a platinum dish and the residue was heated at a temperature 300~320°C. Ammonium chloride and the excess of dimethylglyoxime were sublimed and the potassium was determined gravimetrically as potassium chloride. The phosphate absorbed on the column was eluted with 3N hydrochloric acid, hydrolyzed to orthophosphate by boiling, precipitated with a magnesia mixture, and determined gravimetrically as magnesium pyrophosphate. The solid phase was dissolved in 1N hydrochloric acid, evaporated to dryness, dissolved in water, and neutralized with a dilute solution of sodium hydroxide. The solution thus obtained was treated using the same procedure as in the case of the aqueous phase.

In the process of the reaction with the potassium Kurrol salt, variation of nickel ion concentration was followed by a direct colorimetric method for the nickel ion with a filter of 390 mμ. Various metal ions in aqueous phases were determined as follows: the cobalt(II) ion was determined by the tricarbonato cobalt(III) method[9], the calcium, the magnesium, and the zinc ion were by the chelatometric titration with ethylenediaminetetraacetate, the iron(II) ion was by the permanganometric titration, and copper ion by the iodometric titration. The manganese(II) ion was oxidized with silver nitrate and ammonium persulfate to permanganate, a solution of ammonium iron(II) sulfate, of a known concentration was added, and the excess of iron-(II) was titrated with a standard solution of permanganate. The iron(III) ion was reduced with zinc amalgam to iron(II) and determined by the permanganometric titration. A minute amount of condensed phosphate dissolved in the aqueous solution was determined by the colorimetry[10], after being hydolyzed to orthophosphate.

Results and Discussion

1. X-ray Diffraction Data of the Potassium Kurrol Salt.—Klement and Schmid[11] took the X-ray powder diffraction photographs of potassium Kurrol salt used in his study. Both results in Klement and Schmid's and the present work indicated a good coincidence as shown in Table I. The X-ray pattern of potassium Kurrol salt was not changed by any of the following treatments: Drying at 100° to 110°C for 1 hr., washing with ethanol and ether, and drying in air after being immersed in water for 50 hr.

TABLE I. X-RAY DIFFRACTION DATA OF POTASSIUM KURROL SALT

This work		Klement and Schmid[11]	
Spacing Å	Intensity	Spacing Å	Intensity
6.28	100	6.40	3
5.24	15	5.18	2
5.06	28		
4.50	30	4.54	2
3.75	18	3.92	2
3.45	60	3.42	5
3.35	21		
3.29	30	—	—
3.14	79	3.13	3
3.08	15		
2.83	14	2.82	2
2.74	9	2.74	2
2.68	37	2.64	2
2.58	6	2.55	1
2.26	35	2.25	4
2.21	12	2.20	3
2.10	5	—	—
2.05	3	2.02	2
2.03	3		
1.89	6	1.88	3
1.88	6		
1.80	3	—	—
1.74	5	1.72	2
1.69	3	—	—
1.67	5	—	—
1.64	3	—	—
1.61	3	1.61	2
1.57	5	1.57	2
1.50	4	—	—

2. Non-existence of Tripolyphosphate in the Potassium Kurrol Salt.—About 0.9 g. of the pulverized potassium Kurrol salt was further ground in 100 ml. of ice-water and the suspension was filtered. By this treatment potassium tripolyphosphate, if present, can be washed out of the sample and at the same time the hydrolysis of condensed phosphate may be reduced to a negligible extent. After the filtrate was dried by the use of a freeze-drying machine, the residue was brought into a solution with 0.5 ml. of water. In a two-dimensional paper chromatogram of this solution, there was only a non-moving spot at the original point. This means that the potassium Kurrol salt did not contain any tripolyphosphate or any other shorter chain or ring phosphates and that a minute amount of the potassium Kurrol salt was brought into the solution without intense hydrolysis.

3. Solubility of the Potassium Kurrol Salt.—About 1 g. of the potassium Kurrol salt was

9) M. Mori and M. Shibata, *J. Chem. Soc. Japan, Pure Chem. Soc.* (*Nippon Kagaku Zasshi*), **75**, 1044 (1954).
10) M. Nakamura, *J. Agr. Chem. Soc. Japan* (*Nippon Nogei Kagaku Kai-shi*), **24**, 1 (1950).
11) R. Klement and J. Schmid, *Z. anorg. allgem. Chem.*, **290**, 113 (1957).

put into 1 l. of water and stirred at room temperature (20~23°C). After 1, 2, 3, and 25 hr. the phosphorus content of the phosphate in the solution were determined to be 19, 17, 20, and 23 γ P per ml., respectively. From these values the solubility was calculated to be 0.007 ~0.009 per cent.

4. Qualitative Observation on the Behavior of the Potassium Kurrol Salt toward Aqueous Solutions of Various Metal Ions.—As mentioned previously, potassium Kurrol salt is dissolved in aqueous solutions of sodium salts. To 0.1 g. of the potassium Kurrol salt 10 ml. of a 0.1 M solution of each of the following sodium salts was added; acetate, bromide, carbonate, chloride, cyanate, dihydrogen orthophosphate, monohydrogen carbonate, monohydrogen orthophosphate, nitrate, orthophosphate (normal), oxalate, pyrophosphate, sulfate, and tripolyphosphate. In every case a greater part of the potassium Kurrol salt was dissolved. However, it appeared that the potassium Kurrol salt was more rapidly dissolved in the solutions of ortho-, pyro- and tripolyphosphate in comparison with the other salts.

To 0.1 g. of the potassium Kurrol salt, 10 ml. of 1, 0.5, 0.1, or 0.01 M solution of sodium chloride was added, respectively, where the ratio Na/K was 10, 5, 1, or 0.1. When the ratio was 5, the sample was most easily dissolved. When the ratio was 10, a part of the sample was converted into a gelatinous substance. Probably it was due to salting-out effect.

The results of the qualitative observation on the behavior of the potassium Kurrol salt toward solutions of various metal ions are summarized in Table II. These results were obtained when 0.1 g. of the potassium Kurrol salt was added to 10 ml. of a 0.1 M solution of the metal ion.

Table II. Reactions of potassium Kurrol salt with solutions of metal ions

Metal ion	Reaction
Na^+, NH_4^+	Potassium Kurrol salt is gradually dissolved.
Ca^{2+}, Cr^{3+}, Ag^+	Potassium Kurrol salt forms a lump which has not plasticity.
Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Sn^{2+}	Potassium Kurrol salt forms a gummy substance.
Al^{3+}, Fe^{3+}, Ce^{3+}, Hg^{2+}, Bi^{3+}, Pb^{2+}	Potassium Kurol salt reacts with them very slowly.

5. Reaction between the Potassium Kurrol Salt and Solutions of Nickel Sulfate.—When the potassium Kurrol salt was added to a solution of nickel sulfate, the white crystalline potassium Kurrol salt was gradually converted into a green gummy substance. The absorption of nickel ion was investigated as follows. At a bottom of an Erlenmeyer flask of 300 ml., 1 g. of the ground potassium Kurrol salt was flatly placed and 200 ml. of a 0.0984 M solution of nickel sulfate was added to it. The mixture was kept at 20°C without agitation. The variation of the amounts of the nickel ion absorbed with time was determined by measuring the decrease of the nickel ion concentration in the solution. As shown by the curve A in Fig. 1,

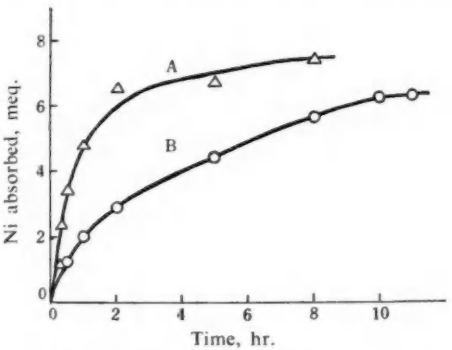


Fig. 1. The variation of the amounts of ion absorbed with time. The initial concentrations of nickel sulfate are 0.0984 M in Curve A and 0.0366 M in Curve B.

after about 8 hr. the reaction reached the equilibrium. When a 0.0366 M solution of nickel sulfate was used, the curve B in Fig. 1 was obtained by a similar experiment. In this case the reaction reached the equilibrium after about 11 hr. After the reaction was equilibrated, the solid phase was removed from the solution, washed quickly with water, and analyzed for potassium, nickel and phosphorus. The amounts of sulfate ion absorbed by the solid phase were negligibly small. The phosphorus contents in the solid phases were 8.50 mg. atom in both cases in comparison with 8.47 mg. atom which was the calculated value of phosphorus content in the initial potassium Kurrol salt. Therefore, all of the phosphorus in the initial sample were assumed to remain in the solid phase in the process of the reaction. As shown in Table III the quantity of the potassium ion which came out of the solid phase was equivalent to the quantity of the nickel ion which went into the solid phase. It was concluded that the reaction mentioned above is a kind of cation-exchange reaction. In the systems of 1 g. of the potassium Kurrol salt and 200 ml. of the 0.0984 M and 0.0366 M solution of nickel sulfate 91 and 74 per cent of potassium ion was exchanged with nickel

TABLE III. CATION-EXCHANGE REACTION BETWEEN POTASSIUM KURROL SALT AND SOLUTIONS OF NICKEL SULFATE

No.	Initial quantity of K^+ ion in the solid phase meq.	Final quantity of K^+ ion in the solid phase meq.	Quantity of K^+ ion which came out of the solid phase		Quantity of Ni^{2+} ion which went into the solid phase	
			meq.	% exchange	meq.	% exchange
A*	8.47	0.81	7.66	90.4	7.68	90.8
B**	8.47	2.16	6.31	74.5	6.24	73.7

*A A reaction between 1 g. of potassium Kurrol salt and 200 ml. of a 0.0984 M solution of $NiSO_4$ for 8 hr. at 20°C.

**B A reaction between 1 g. of potassium Kurrol salt and 200 ml. of a 0.0366 M solution of $NiSO_4$ for 11 hr. at at 20°C.

TABLE IV. PROPERTIES OF THE NICKEL-SUBSTITUTED PRODUCTS HEATED AT VARIOUS TEMPERATURES

Product	Heated at, °C	Appearance	For X-rays	Two-dimensional paper chromatographic information
A	100~110	green, transparent	amorphous	—
B	300	dark brown, powder	amorphous slightly crystalline	—
C	600	light yellow, powder	crystalline	non-moving spot indicating long-chain phosphate
D	1000	yellowish green, powder	crystalline	chain series containing ortho-, pyro-, tripolyphosphate, etc., ring series containing trimeta-, tetrameta,, pentametaphosphate, etc. and non-moving spot
E	1200	dark yellow, powder	crystalline	chain series containing ortho-, pyro-, tripolyphosphate, etc. and non-moving spot

ions in 8 and 11 hr., respectively.

In order to confirm the reversibility of the cation-exchange reaction, a green product obtained by the reaction between 1 g. of the potassium Kurrol salt and 200 ml. of a 0.1052 M solution of nickel sulfate for 8 hr. at 20°C was subjected to react with 50 ml. of a 0.2 M solution of potassium chloride for 40 hr. at 20°C. Before and after the reverse reaction, the solid phase was analyzed for potassium, nickel and phosphorus. Phosphate was not dissolved in the process of this reaction. The quantity of the potassium ion which went into the solid phase was 1.48 meq. and the quantity of the nickel ion which came out of the solid phase was 1.47 meq. This fact indicates that the reaction is reversible. The rate of the reverse reaction was slower than that of the ordinary reaction, since the surface area of the primary product was smaller than that of the initial potassium Kurrol salt. The equilibration of the reverse reactoin was attained after about 40 hr.

6. Properties of the Nickel-substituted Product.—The nickel-substituted product in which about 90 per cent of the initial amount of the potassium ion is replaced by the nickel ion is green-colored and gummy. It is quite similar to chewed chewing-gum. The green product is gradually dissolved into a large amount of water. A similar product can be made in a short time by dissolving potassium Kurrol salt in a dilute solution of sodium chloride or sodium tripolyphosphate and adding a concentrated solution of nickel sulfate. This fact may be due to salting-out effect.

The variation in the properties of the green product by heating was investigated and the results are summarized in Tablle IV. The green primary product and the product A were completely amorphous for X-rays. The product B was practically amorphous for X-rays, but it contained a small amount of crystalline substance. The products C, D and E were all crystalline for X-rays and their X-ray patterns were different from one another. The products A and B were soluble in mineral acids, but the products C, D, and E were soluble in mineral acids only with difficulty. The product E was not dissolved even by heating it with 6 N hydrochloric acid, 6 N nitric acid, aqua regia, or 3 N sodium hydroxide. Each 0.1 g. of the products C, D and E was well mixed with 1 g. of Amberlite IR-120 resin in sodium form (100~200 mesh) in 8 ml. of water. After centrifugation the supernatant was concentrated

Table V. Cation-exchange reaction between potassium Kurrol salt and solutions of various metal ions

Metal salt	Concn.	pH, initial	Quantity of metal ion exchanged	Exchange capacity at the end of the reaction	% exchange
	M		meq.	meq.	
$MgCl_2$	0.0946	5.6	7.08	8.45	83.8
$CaCl_2$	0.0981	3.9	6.95	8.43	82.4
$MnCl_2$	0.1300	3.0	7.84	8.32	94.2
$FeSO_4$	0.0928	1.3	7.59	8.39	90.5
$Fe_2(SO_4)_3$	0.1568	0.8	3.80	7.35	51.7
$CoCl_2$	0.0987	4.7	7.39	8.46	87.3
$NiSO_4$	0.0984	5.6	7.68	8.47	90.8
$CuSO_4$	0.1006	4.3	5.03	5.77	87.2
$ZnCl_2$	0.0910	2.1	7.92	8.46	93.7

at room temperature. Two-dimensional paper chromatography for the solution was carried out. The results are shown in Table IV. Although only minute parts of the products C, D and E were brought into the solutions, the paper chromatographic data suggested the difference of the chemical compositions of these products.

7. Exchange-reactions of Various Metal Ions. —In conformity to the procedure used for the nickel ion, 1 g. of the potassium Kurrol salt was subjected to react with 200 ml. of about 0.09~0.16 M solution of each of the following metal ions for 8 hr. at 20°C: magnesium, calcium, manganese(II), iron(II), iron(III), cobalt(II), copper(II) and zinc. After the exchange reactions, the amounts of phosphate dissolved in the solution and the decreases in the metal ion concentrations were measured. With the aid of these measurements, percentages of exchange based on millieqivalent of cations were calculated as shown in Table V. Only in the case of copper(II) sulfate a large amount of the initial potassium Kurrol salt was dissolved in the course of the reaction. Except for iron(III), percentages of exchange for all cations investigated in the present work were in the range 82 to 94.

Summary

Pure crystalline potassium Kurrol salt was prepared and its X-ray pattern was compared with that obtained by Klement et al. The solubility of the potassium Kurrol salt in water was 0.007~0.009 per cent at room temperature. Qualitative observation was made for the reactions of the potassium Kurrol salt with various metal ions. Therefore was an optimum concentration of sodium chloride to dissolve the potassium Kurrol salt. The investigation of reactions of the potassium Kurrol salt in a solid state with solutions of nickel sulfate indicated that the reaction is a cation-exchange reaction between potassium and nickel ions. It was also found that the reaction is reverssible. The nickel-substituted product is green-colored and gummy. Some properties of the substances obtained by heating the above green product were studied. Exchange reactions of potassium Kurrol salt with various metal ions were investigated. Percentages of exchange for magnesium, calcium, manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc were all in the range 82 to 94 under the conditions used in the present work.

The authors are indebted to Professor T. Kiba for his continued encouragement.

Department of Chemistry
Faculty of Science
Kanazawa University
Kanazawa

Distribution of Unpaired π-Electron in Some Semiquinone Ions

By Yoshio MATSUNAGA

(Received May 2, 1960)

The hyperfine structure (hfs) of the electron spin resonance (ESR) spectra of free radicals in the dissolved state arises from the interaction between the magnetic moment of the unpaired π-electron and the magnetic moments of the protons and some other magnetic nuclei in the molecule. Based on the spectra of *o*- and *p*-benzosemiquinone ions McConnell has suggested that the magnitude of ring proton splitting constant a_j is approximately proportional to the density of unpaired π-electron ρ_j on the adjacent aromatic carbon atom j given by a simple MO treatment, and proposed the relation $a_j=34\rho_j$[1]. Later he has developed a theoretical study in terms of configurational interaction and concluded that the above-mentioned empirical relation can be used for practical calculation[2]. This approximation has been applied successfully to the interpretation of hfs of ESR spectra of a number of alternant aromatic hydrocarbon monopositive and mononegative ions[3,4].

McConnell has used a set of parameters $\alpha_O=\alpha+\beta$ and $\beta_{CO}=\beta$ in his simple MO treatment of benzosemiquinone ions[1]. These values have been originally proposed for the oxygen atoms and the carbon-oxygen bonds in neutral quinone molecule[5], and the effect of negative charge on the magnitude of these parameters has not been taken into consideration in the treatment of semiquinone ions. Therefore, it seemed to be desirable to find a correct set of parameters for the extension of theoretical work to the semiquinone ions with more complicated molecular structure. The MO treatment with such a set of parameters might be very helpful to the analysis of hfs of ESR spectra of semiquinone ions. In the previous paper the author has attempted to estimate the required parameters based on the frequencies of the C-O stretching vibration in alkali salts of *p*-benzo- and *p*-biphenosemiquinones and obtained a set of $\alpha_O=\alpha+(1/3\sim1/2)\beta$ and $\beta_{CO}=\beta$[6]. Here we wish to present the results of simple MO treatment with the suggested parameters and compare with the experimental results for several semiquinone ions.

1) H. M. McConnell, *J. Chem. Phys.*, **24**, 632 (1956).
2) M. M. McConnell, ibid., **28**, 1188 (1958).
3) E. de Boer and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 4549 (1958).
4) A. Carrington, F. Dravnieks and M. C. R. Symons, *J. Chem. Soc.*, **1959**, 947.
5) M. G. Evans, J. Gergely and J. de Heer, *Trans. Faraday Soc.*, **45**, 312 (1949).

Method of Calculation

The calculations in the present paper were carried out by the simple LCAO MO method. The density of unpaired π-electron at each carbon atom was approximated by the square of the coefficient of its $2p$ function in the singly occupied MO. The coulomb integrals for carbon atoms were assumed to be α, and the exchange integrals were taken as β including that for C–O bonds. The coulomb integral for the oxygen atoms was assumed to be $\alpha+(1/2)\beta$ or $\alpha+(2/3)\beta$. The former value was taken from the previous paper[6] and the latter was estimated by the following method. Naphthosemiquinone ion gives a spectrum of three quintets, therefore the density of unpaired π-electron on the aromatic carbon atoms 5 and 5′ is practically equal to that on the carbon atoms 6 and 6′ (see structural formula). The singly occupied MO of this semiquinone ion is antisymmetric. Accordingly, if we assume $\beta_{CO}=\beta$, the magnitude of the coulomb integral for the oxygen atoms $\alpha_O=\alpha+\delta\beta$ can be determined by the system of equations for the coefficient c_j of $2p$ function at carbon atom j;

$$\begin{aligned}
&(y+\delta)c_1+c_3=0\\
&(y-1)c_2+c_3=0\\
&c_1+c_2+yc_3+c_4=0\\
&c_3+(y-1)c_4+c_5=0\\
&c_4+yc_5+c_6=0\\
&c_5+(y-1)c_6=0,
\end{aligned}$$

where $y=(\alpha-E)/\beta$, and the normalizing condition $\sum c_j^2=1$. If the coefficients of $2p$ function at the carbon atoms 5 and 6 are supposed to be exactly equal to each other, we obtain $\alpha_O=\alpha+(2/3)\beta$. We used $a_j=32\rho_j$ throughout this paper instead of $a_j=34\rho_j$ proposed by McConnell for semiquinone ions simply by the reason that the former seems to fit better with the experimental results. The structural formula and the numbering of oxygen and carbon atoms chosen for convenience are summarized in Fig. 1.

6) Y. Matsunaga, *Can. J. Chem.*, to be published.

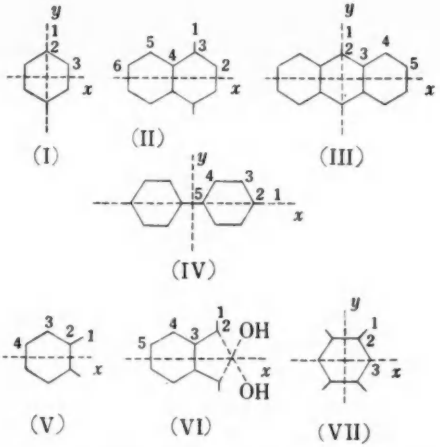


Fig. 1. Structural formula and numbering of oxygen and carbon atoms.

Results and Discussion

***p*-Benzosemiquinone Ion (I).**—This free radical ion has four equivalent protons and gives a predicted quintet with intensity ratios 1:4:6:4:1. The splitting constant has been reported as 2.37±0.01 oersteds by Adams, Blois, and Sands[7]. The densities of unpaired π-electron given by a simple MO treatment and the predicted splitting constant are presented in Table I for various values of $\delta=(\alpha_O-\alpha)/\beta$. Since the magnitude of splitting constant depends only slightly on the value of δ, it is hard to tell which value of δ gives the best result.

TABLE I. UNPAIRED ELECTRON DENSITIES (ρ_j) AND SPLITTING CONSTANT (a_3 IN OERSTED) FOR *p*-BENZOSEMIQUINONE ION

δ	ρ_1	ρ_2	ρ_3	a_3
0	0.332	0.032	0.068	2.18
1/2	0.286	0.071	0.071	2.27
2/3	0.264	0.088	0.074	2.37
1	0.221	0.123	0.078	2.50

Naphthosemiquinone Ion (II).—The splitting constants have been reported as 3.22±0.03 oersteds for the ring protons attached to the positions 2 and 2′ and 0.57±0.03 oersteds for those 5, 5′, 6 and 6′. The results of calculation are given in Table II. With a difference of 0.1 oersted it is difficult to distinguish experimentally the splittings due to a_5 and a_6, therefore both of the results obtained assuming $\delta=1/2$ and 2/3 may be considered to be in good agreement with the observed values.

It has been shown that the hf splitting constant for a methyl proton is related to the unpaired π-electron density on the carbon atom, to which the methyl group is attached, by a formula of the same type as for a ring proton[8,9]. Besides the proportional constants for these two kinds of protons seem to be nearly the same. As the unpaired electron density in a methyl group is only in the order of 0.01, we may expect the distribution of unpaired π-electron is not much modified by methyl substitution. Therefore, the magnitude of a methyl proton splitting may be close to that of the ring proton attached to the corresponding carbon atom in the unsubstituted free radical ion. The following splitting constants could be assigned for monomethylnaphthosemiquinone ion; 3.2 oersteds for the methyl group attached to the position 2, 2.6 oersteds for the ring proton attached to the position 2′, and 0.6 oersteds for the remaining four ring protons. The spectrum consists of twenty-four lines as shown in Fig. 2. For dimethyl-derivative 2.3 oersteds for the six protons in the methyl groups attached to the positions 2 and 2′ and 0.57 oersteds for the ring protons have been assigned by Vivo[10]. Contrary to Vivo's result, an expected quintet with a spacing of

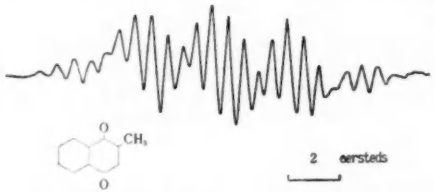


Fig. 2. Electron spin resonance spectrum of monomethylnaphthosemiquinone ion.

TABLE II. UNPAIRED ELECTRON DENSITIES (ρ_j) AND SPLITTING CONSTANTS (a_j IN OERSTED) FOR NAPHTHOSEMIQUINONE ION

δ	ρ_1	ρ_2	ρ_3	ρ_4	ρ_5	ρ_6	a_2	a_5	a_6
0	0.307	0.097	0.040	0.029	0.008	0.019	3.10	0.26	0.61
1/2	0.249	0.099	0.083	0.026	0.019	0.023	3.17	0.61	0.74
2/3	0.225	0.100	0.100	0.025	0.025	0.025	3.20	0.80	0.80
1	0.175	0.103	0.132	0.022	0.039	0.030	3.30	1.25	0.96

7) M. Adams, M. S. Blois, Jr. and R. H. Sands, *J. Chem. Phys.*, **28**, 774 (1958).
8) C. B. Chesnut, ibid., **29**, 43 (1958).
9) A. C. McLachlan, *Mol. Phys.*, **1**, 233 (1958).
10) J. L. Vivo, Dissertation, University of Minnesota, 1956.

0.6 oersteds was found in the case of dichloronaphthosemiquinone ion. We may conclude that the ring protons at 5 and 6 are nearly equivalent in all of the examined derivatives.

The semiquinone ion formed on reduction of hydroxynaphthoquinone in alkaline medium has an ionized oxygen atom attached to the position 2. The effect of this substituent is so strong that the distribution of unpaired π-electron in naphthosemiquinone ion is completely changed. The spectrum consists of partially resolved two doublets (1.6 and 1.8 oersteds) instead of two quintets. By comparison with the well-resolved two doublets with 1.5 and 1.9 oersteds given by the semiquinone ion from hydroxychloronaphthoquinone, in which the chlorine atom can be considered inactive to hf splitting, it appears that the observed hfs is entirely due to the interaction between unpaired electron and two protons among four attached to the positions 5, 5′, 6 and 6′ (see Fig. 3).

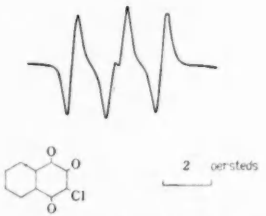


Fig. 3. Electron spin resonance spectrum of the semiquinone ion from hydroxychloronaphthoquinone.

Anthrasemiquinone Ion (III).—This semiquinone ion gives a spectrum of thirteen lines resulting from one set of four equivalent protons and another of four. The splitting constant for one set must be 1.0 oersted and for the other 0.5 oersteds. However, without further information we cannot determine which of the two possible assignments is responsible. The results by simple MO treatment with the proposed parameters suggest that the proton at 5 and its three equivalents give the larger splitting.

TABLE III. UNPAIRED ELECTRON DENSITIES (ρ_j) AND SPLITTING CONSTANTS (a_j IN OERSTED) FOR ANTHRASEMIQUINONE ION

δ	ρ_1	ρ_2	ρ_3	ρ_4	ρ_5	a_4	a_5
0	0.277	0.050	0.046	0.010	0.030	0.32	0.96
1/2	0.214	0.098	0.042	0.021	0.031	0.67	0.99
2/3	0.191	0.115	0.040	0.026	0.031	0.83	0.99
1	0.143	0.143	0.036	0.036	0.036	1.15	1.15

Biphenosemiquinone Ion (IV).—As shown in Table IV, the splitting due to the proton at 3 is expected to be twice or a little more larger than that due to the proton at 4. Unfortunately this free radical ion was found too unstable to be examined by our spectrometer. Tetramethylbiphenosemiquinone ion has four methyl groups attached to the position 3 and its equivalents and gives a spectrum of twenty-one lines with a spacing of 0.78 oersteds[11]. This pattern could be explained using the splitting constants 2.34 oersteds for the ring protons and 0.78 oersteds for the methyl protons as well as using 0.78 oersteds for the ring protons and 1.56 oersteds for the methyl protons. The theoretical results given in Table IV are definitely favorable to the latter assignment.

TABLE IV. UNPAIRED ELECTRON DENSITIES (ρ_j) AND SPLITTING CONSTANTS (a_j IN OERSTED) FOR BIPHENOSEMIQUINONE ION

δ	ρ_1	ρ_2	ρ_3	ρ_4	ρ_5	a_3	a_4
0	0.278	0.005	0.067	0.011	0.060	2.14	0.35
1/2	0.227	0.033	0.062	0.023	0.071	1.98	0.74
2/3	0.202	0.045	0.060	0.028	0.077	1.92	0.90
1	0.152	0.072	0.056	0.038	0.088	1.79	1.22

***o*-Benzosemiquinone Ion (V).**—The three triplets observed in the ESR spectrum of this radical ion have been analyzed by Hoskins[12]. The major splitting has been attributed to the protons attached positions 4 and 4′ and the minor one to those at 3 and 3′. The values have been estimated as 3.65 ± 0.04 and 0.95 ± 0.04 oersteds by Adams et al.[7] Both of the splitting constants calculated using $\delta=1/2$ and 2/3 were found in serious disagreement with the experimetnal ones. Since our parameters seemed not applicable to *o*-semiquinone ions, we attempted to estimate a new one which gives a ratio of $c_4^2/c_3^2=4$ in the present case. Although the value thus estimated as high as 1.611 might suggest that a more refined model is required for the MO treatment of *o*-semiquinone ion, it must be noted that the calculated splitting constants are in good agreement with the observed ones. The unpaired π-electron distribution cited in the last line of Table V is taken from Kuboyama's work on *o*-quinones[13]. As we may expect for the reasons discussed above, his results obtained with the following parameters for neutral quinone molecule predict the splitting constants not far from the experimental ones; $\alpha_O=\alpha+1.3\beta$, $\alpha_2=\alpha+0.2\beta$, $\beta_{22'}=0.8\beta$, $\beta_{23}=\beta_{44'}=0.9\beta$, $\alpha_3=\alpha_4=\alpha$ and $\beta_{12}=\beta_{34}=\beta$.

11) Y. Matsunaga and C. A. McDowell, *Can. J. Chem.*, to be published.
12) R. H. Hoskins, *J. Chem. Phys.*, **23**, 1975 (1955).
13) A. Kuboyama, This Bulletin, **32**, 1226 (1959).

Table V. Unpaired electron densities (ρ_j) and splitting constants (a_j in oersted) for *o*-benzosemiquinone ion

δ	ρ_1	ρ_2	ρ_3	ρ_4	a_3	a_4
0	0.295	0.026	0.113	0.067	3.62	2.14
1/2	0.286	0.071	0.071	0.071	2.27	2.27
2/3	0.272	0.090	0.062	0.076	1.98	2.43
1	0.234	0.128	0.049	0.089	1.57	2.85
1.611	0.155	0.192	0.031	0.123	0.99	3.94
Kuboyama*	0.191	0.176	0.032	0.101	1.02	3.23

* See Ref. 13.

Semiquinone Ion from Ninhydrin (VI). — Adams et al. have observed that ninhydrin on reduction gives a spectrum of three triplets due to the two pairs of equivalent protons on the aromatic ring, and estimated the splitting constants to be 1.95±0.04 and 1.59±0.04 oersteds[7]. The conjugated system of this radical ion was considered to be similar to that of *o*-divinylbenzene and examined by the simple MO method changing the magnitude of δ. The results suggest that the larger splitting is attributed to the protons attached to the positions 5 and 5', and the value of δ close to 1.6 is again required for quantitative agreement with the experimental results.

Table VI. Unpaired electron densities (ρ_j) and splitting constants (a_j in oersted) for the semiquinone ion from ninhydrin

δ	ρ_1	ρ_2	ρ_3	ρ_4	ρ_5	a_4	a_5
0	0.232	0.071	0.111	0.014	0.071	0.45	2.27
1/2	0.185	0.132	0.093	0.027	0.063	0.86	2.02
2/3	0.167	0.152	0.089	0.031	0.061	0.99	1.95
1	0.132	0.186	0.080	0.041	0.061	1.31	1.95
1.6	0.084	0.231	0.069	0.055	0.061	1.76	1.95

Semiquinone Ion from Dihydroxy-*p*-benzoquinone (VII). — It has been found that the ring proton splitting changes from 1.83 oersteds in dimethyl-*p*-benzosemiquinone ion to 0.30 oersteds in dimethoxy-derivative[11]. This considerable decrease suggests the localization of unpaired π-electron on the oxygen atoms in the methoxyl groups. We extended here our measurements to the highly symmetric semiquinone ion formed on reduction of dihydroxy-*p*-benzoquinone. Although we do not know the correct value of δ for this triply charged semiquinone ion, the value must be in the range from −1 for negatively charged oxygen to +1 for the oxygen atom in carbonyl group[14]. The singly occupied level predicted by a simple MO treatment for this semiquinone ion is antisymmetric with respect to the *x*-plane. Therefore, no unpaired π-electron density is found on the carbon atoms to which the ring protons are attached and we may expect no hfs in the ESR spectrum of the present radical ion. The small splitting due to the ring protons observed in the case of dimethoxy-*p*-benzosemiquinone ion may be correlated with the difference between the electronegativities for two kinds of oxygen atoms.

Contrary to the expectation, on reduction with sodium dithionate dihydroxy-*p*-benzoquinone dissolved in a mixture of pyridine, ethylene glycol, and 2 N pottasium hydroxide (1:2:1 by volume) shows a triplet with a spacing of 0.78 oersteds. If we substitute the two ring protons with chlorine or bromine atoms, the semiquinone ion gives an expected single line spectrum. Apparently there is the ring proton splitting in the ESR spectrum of the radical ion formed by reduction of dihydroxy-*p*-benzoquinone. The unpaired π-electron density on the adjacent carbon atoms must be as high as 0.02. Therefore, we may conclude that a single configuration MO treatment does give neither the correct symmetyr of energy level nor the correct distribution of unpaired π-electron for the present radical. A similalr disagreement as to the symmetry of energy level has been reported by de Boer and Weissman in the case of pyrene negative ion[3].

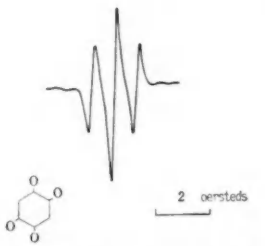


Fig. 4. Electron spin resonance spectrum of the semiquinone ion from dihydroxy-*p*-benzoquinone.

Summary

The distribution of unpaired π-electron was calculated by the simple MO method using the proposed parameters $\alpha_O = \alpha + (1/2)\beta$ and $\alpha + (2/3)\beta$ for six semiquinone ions. The calculated splitting constants for the ring protons in *p*-benzo- and naphtho-semiquinone ions were found in good agreement with the experimental ones and the MO treatment with the proposed parameters seemed to be very helpful to the analysis of the hfs of ESR spectra of anthra- and bipheno-semiquinone ions. In the case of *o*-semiquinone ion, a much higher value of α_O was required to obtain quantitative agreement. The assignment of splitting constants was

14) H. H. Jaffe, *J. Am. Chem. Soc.*, **77**, 4448 (1955).

attempted for the semiquinone ion from ninhydrin. It was found that the simple MO method fails to predict the symmetry of the singly occupied MO in the semiquinone ion formed on reduction of dihydroxy-*p*-benzoquinone. In addition the ESR spectra of the semiquinone ions from methyl- and hydroxynaphthoquinones etc. were described.

The spectra quoted in this paper were obtained at the University of British Columbia during the tenure of a National Research Council of Canada Postdoctorate Fellowship. The author wishes to express his sincere thanks to Professor C. A. McDowell for his generous keep and hospitality.

Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo

Hydrogen Peroxide Oxidation. IV. A New Rearrangement Reaction of Phenyl Alkyl Ketones by Selenium Dioxide Catalyst[1]

By Noboru SONODA and Shigeru TSUTSUMI

(Received May 10, 1960)

In the previous papers[2,3] we reported the rearrangement reactions of dialkyl ketones by selenium dioxide catalyzed oxidation with hydrogen peroxide, and now the present paper deals with a similar study using several phenyl alkyl ketones.

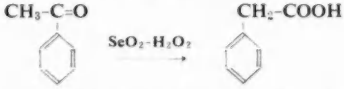
The rearrangement reaction mode of a dialkyl ketone is shown generally as below;

$$\begin{matrix} R_1 \\ R_2 \end{matrix}\!\!>\!CH\text{-}C\text{-}R_3 \xrightarrow[\text{in } \textit{tert}\text{-butyl alcohol}]{SeO_2\text{-}H_2O_2} R_2\text{-}\overset{R_1}{\underset{R_3}{C}}\text{-}COOH \qquad (1)$$

R_1, R_2 = H or alkyl, R_3 = alkyl

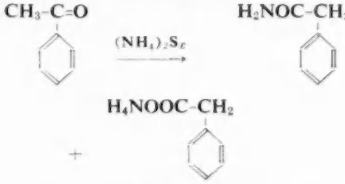
where either of the two alkyl groups R_1R_2CH- and R_3, can migrate onto the α-carbon atom of the other alkyl group so that the two isomeric acids containing the same number of carbon atoms as original ketone are produced when unsymmetrical ketone is used. In the case of phenyl alkyl ketone, only the rearrangement of the phenyl group is possible, because the phenyl group does not possess an α-hydrogen atom which may be substituted by the migrating alkyl group. Thus, the α-phenyl carboxylic acids are synthesized from phenyl alkyl ketones by the oxidation with selenium dioxide-hydrogen peroxide reagent.

For example, when acetophenone was treated with hydrogen peroxide in *tert*-butyl alcohol in the presence of a small amount of selenium dioxide as catalyst at about 80~82°C, phenyl acetic acid was isolated from the reaction products as well as some cleavaged products.



(2)

Synthesis of phenyl acetic acid derivatives from acetophenone had also been undertaken by Willgerodt[4] showing that phenyl acetamide and ammonium phenyl acetate were obtained by the oxidation of acetophenone with ammonium polysulfide. But in the Willgerodt reaction[5] no change of carbon skeleton was observed because of the reduction of the carbonyl group to the methylene group and the oxidation of the methyl group to carbonamide or salt of carboxylic acid.

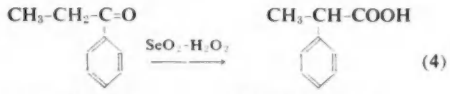


(3)

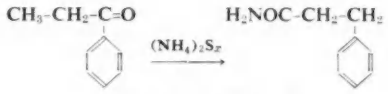
On the other hand the production of phenyl acetic acid from acetophenone by selenium

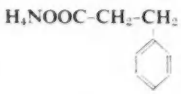
1) Presented at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April 2, 1959.
2) N. Sonoda and S. Tsutsumi, This Bulletin, **32**, 505 (1959).
3) N. Sonoda, T. Yamaguchi and S. Tsutsumi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **63**, 737 (1960).
4) C. Willgerodt, *Ber.*, **21**, 534 (1888); C. Willgerodt and F. H. Merk, *J. prakt. Chem.*, **80**, 192 (1909).
5) For a review of the Willgerodt reaction, see (a) M. Carmack, "Organic Reactions", Vol. III, John Wiley & Sons, Inc., New York, N. Y. (1946), pp. 83-107; (b) R. Wegler, E. Kühle and W. Schäfer, *Angew. Chem.*, **70**, 351 (1958).

dioxide catalyzed hydrogen peroxide oxidation is clearly based on the migration of the phenyl group to the methyl carbon atom. An evidence of the rearrangement was shown by the fact that α-phenyl propionic acid was produced by the phenyl migration when phenyl ethyl ketone was treated under the reaction condition similar to that of acetophenone, whereas β-phenyl propionic acid derivatives were formed from phenyl ethyl ketone under the Willgerodt reaction condition[4].



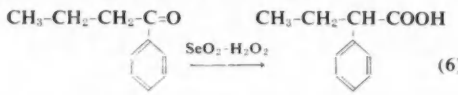
(4)





(5)

In a similar manner, phenyl *n*-propyl ketone was oxidized with selenium dioxide-hydrogen peroxide reagent to give α-phenyl butyric acid.



(6)

These facts suggest that similar treatment may be generally applicable to the other aryl alkyl ketones.

The reactivity of phenyl alkyl ketones was apparently lower than that of dialkyl ketones[2,3]. The yield of the rearrangement products was only about 10 per cent based on the treated ketones in spite of using an excess amount of hydrogen peroxide, and fairly good recovery of starting ketones was observed in all the cases.

On the other hand, oxidative cleavage was also observed. Benzoic acid was isolated as a main cleavage product in a comparable yield to the rearrangement product and phenol was identified as its tribromide in all cases. Aliphatic acids derived from the aliphatic fragments of the ketones or oxidative decomposition product[6] of *tert*-butyl alcohol used as solvent were also detected by gaschromatography. These products are listed in Table I.

We have proposed the probable mechanism[2] of these rearrangement reactions, which comprise the enol formation of the ketones

Table I. Cleavage products from oxidative reaction of phenyl alkyl ketones

Reactants	Products confirmed	Yield %
Acetophenone	Benzoic acid	12.3
	Phenol	trace
	Acetic acid[a]	—
	Propionic acid[b]	—
Phenyl ethyl ketone	Benzoic acid	4.1
	Phenol	trace
	Acetic acid	—
	Propionic acid	—
Phenyl *n*-propyl ketone	Benzoic acid	4.9
	Phenol	trace
	Propionic acid	—
	n-Butyric acid	—

a) Formic acid was assumed to be present, but was not detected.
b) This propionic acid was supplied from the solvent.

followed by the attack of peroxyselenious acid as the most possible active species. Since peroxyselenious acid is a kind of peracid, it is reasonable to believe that the Baeyer-Villiger oxidation[7] may be accompanied in this reaction system. Formation of phenol and aliphatic acid from the corresponding ketone may be interpreted as results of hydrolysis of the phenyl ester produced by the Baeyer-Villiger reaction. In addition, the other cleavage path is assumed to be present, because alkyl benzoate will not be formed from phenyl alkyl ketone[7] under the Baeyer-Villiger reaction condition so that benzoic acid may not be the reaction product via the Baeyer-Villiger oxidation.

Experimental[8]

Oxidative Reagent.—Selenium dioxide-hydrogen peroxide reagent was prepared in the same manner as previously described[2]. This reagent includes 2.0 g. of selenium dioxide and 1.0 mol. of hydrogen peroxide in about 500 ml. of *tert*-butyl alcohol solution.

Oxidation of Acetophenone.—To a 100 ml. of the selenium dioxide-hydrogen peroxide reagent (0.4 g. of selenium dioxide and 0.2 mol. of hydrogen peroxide) was added 12.0 g. (0.1 mol.) of acetophenone, and the resulting mixture was heated to 80~82°C for 17 hr. The reaction mixture turned red during the oxidation. The mixture was distilled to remove the solvent and the small amount of metallic selenium deposited was filtered off. The filtrate was poured into 200 ml. of ether, and the ethereal solution was extracted first with saturated sodium bicarbonate solusion (A) and then with 8% sodium hydroxide solution (B). After the ethereal solution was dried over anhydrous sodium sulfate,

6) Propionic acid was partly produced from acetone which was formed by the decomposition of *tert*-butyl hydroperoxide or di-*tert*-butyl peroxide being furnished by the oxidation of *tert*-butyl alcohol used as solvent. This reaction path was already confirmed (see Ref. 2).

7) C. H. Hassall, "Organic Reactions", Vol. IX, John Wiley & Sons, Inc., New York, N. Y. (1957), p. 73-106.
8) The boiling and melting points are uncorrected.

the ether was removed and the residue was distilled under reduced pressure; 6.6 g. of neutral substance, consisting mainly of unreacted acetophenone, was obtained, b. p. 62~65°C (4 mmHg), 2,4-dinitrophenyl-hydrazone of this fraction melted at 245~246°C (lit.[9] m. p. 247~248°C) and mixed melting point with an authentic sample (m. p. 245~246°C) showed no depression.

The sodium bicarbonate solution A was acidified with 3 N hydrochloric acid and was extracted with ether. After the ethereal solution was dried over anhydrous sodium sulfate, the ether was removed by distillation and the residue was distilled under reduced pressure. Acetic acid and propionic acid were identified in the low boiling products by gaschromatography: column, tricresylphosphate; column temperature, 140°C; carrier gas, H_2; flow rate of H_2, 40 ml./min. The fraction boiling between 112~122°C (4 mmHg), which solidified at once, was collected. This gave 2.8 g. of a mixture of acids. A small portion of the mixture was recrystallized from hot water, and a mixture of two kinds of crystalline solids was obtained. One of them was white plate, phenyl acetic acid, which was separated as floats over the surface of water by shaking. After further recrystallization from petroleum ether, a sample (m. p. 75.5~76°C) was obtained (lit.[10] m. p. 76°C), mixed melting point with an authentic sample was not depressed. The yield of phenyl acetic acid was 9.6% based on the used ketone calculated from ultraviolet spectrum of the mixture of acids.

Found: C, 70.65; H, 6.02. Calcd. for $C_8H_8O_2$: C, 70.57; H, 5.92%.

Benzoic acid, white needle crystals from hot water, was obtained as residue after removal of phenyl acetic acid; the melting point and mixed melting point with an authentic sample was 121°C (lit.[10] m. p. 121°C); the yield was 12.3% calculated from the ultraviolet spectrum.

The sodium hydroxide solution B was acidified and extracted with ether. After the ethereal solution was dried over anhydrous sodium sulfate, the ether was removed by distillation. On distillation of the residual brown oil under reduced pressure, 0.15 g. of phenol was isolated; the tribromide was prepared which melted at 94°C (lit.[10] m. p. 95°C), mixed melting point with an authentic sample showed no depression.

Oxidation of Phenyl Ethyl Ketone.—To a 100 ml. of the selenium dioxide-hydrogen peroxide reagent (0.4 g. of selenium dioxide and 0.2 mol. of hydrogen peroxide) was added 13.4 g. (0.1 mol.) of phenyl ethyl ketone, and the reaction was carried out at 80~82°C for 20 hr. The reaction products were separated in the same manner as described for the oxidation of acetophenone.

Uureacted phenyl ethyl ketone (9.1 g.) was recovered from the neutral part; b. p. 70~73°C (5 mmHg); 2.4-dinitrophenylhydrazone of this fraction melted at 191~192°C (lit.[10] 191°C), mixed melting point with an authentic sample showed no depression.

Acetic acid and propionic acid were identified in the acidic part by the gaschromatography. A mixture of acids, 2.2 g. of oily product of b. p. 115~120°C (3 mmHg), was obtained. After a portion of this product was cooled to 0°C, a crystalline solid deposited was collected on a filter and was purified by recrystallization from petroleum ether to give benzoic acid. The melting point and mixed melting point with an authentic sample was 120~121°C (4.1% yield calculated from ultraviolet spectrum of the mixture of acids). The filtrate was an oily product, which was proved to be α-phenyl propionic acid (11.3% yield). The amide was prepared according to the usual procedure[10] and was recrystallized from benzene, melting at 92.5~93°C (lit.[11] 93°C).

Found: C, 72.34; H, 7.58; N, 9.57. Calcd. for $C_9H_{11}NO$: C, 72.45; H, 7.43; N, 9.39%.

The presence of phenol was identified in the phenolic part by the ferric chloride test.

Oxidation of Phenyl *n*-Propyl Ketone.—To a 100 ml. of the selenium dioxide-hydrogen peroxide reagent (0.4 g. of selenium dioxide and 0.2 mol. of hydrogen peroxide) was added 14.8 g. (0.1 mol.) of phenyl *n*-propyl ketone, and the reaction was carried out at 80~82°C for 24 hr. The reaction products were separated in the same manner as described for the oxidation of acetophenone.

The unreacted phenyl *n*-propyl ketone (10.2 g.) was recovered from the neutral part; b. p. 104~108°C (14 mmHg); 2,4-dinitrophenylhydrazone melted at 190~191°C (lit.[9] 191~192°C), mixed melting point with an authentic sample was not depressed.

Propionic acid and butyric acid were identified by the gaschromatography. On distillation, 1.5 g. of a mixture of acids, b. p. 105~110°C (1 mmHg), was obtained. After the mixture was allowed to stand at room temperature for several hours, the crystalline product deposited was filtered and recrystallized from hot water to give 0.6 g. (4.9% yield) of benzoic acid, m. p. 121°C. The filtrate, 0.7 g. (4.3% yield) of α-phenyl butyric acid, froze to a crystalline solid, which melted slightly above room temperature (lit.[12] m. p. 43°C). A redistilled sampe showed neutral equivalent 162; calculated for $C_{10}H_{12}O_2$: 164.2. The amide was prepared according to the usual procedure[10] and was recrystallized from benzene-ligroin, melting at 83~84°C (lit.[13] 84°C). The phenol was isolated from the phenolic part, 0.2 g.; the tribromide melted at 94°C (lit.[10] 95°C), mixed melting point with an authentic sample showed no depression.

Summary

1) Selenium dioxide catalyzed oxidation of phenyl alkyl ketone with hydrogen peroxide in *tert*-butyl alcohol gave α-phenyl carboxylic acid which was produced by the rearrangement of the phenyl group to the α-carbon atom as shown by Eqs. 2, 4 and 6.

9) G. D. Johnson, *J. Am. Chem. Soc.*, **75**, 2720 (1953).

10) R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds", 4th Ed., John Wiley & Sons, Inc., New York, N. Y. (1956).

11) J. A. King and F. H. H. McMillan, *J. Am. Chem. Soc.*, **68**, 635 (1946).

12) M. M. Rising and T. W. Zee, *J. Am. Chem. Soc.*, **50**, 1211 (1928).

13) *Beilstein*, **9** II, p. 356, Springer-Verlag, Berlin (1946).

Therefore, the reaction mode is quite different from the Willgerodt reaction. The fact described above suggests that similar treatment may be generally applicable to the other aryl alkyl ketones.

2) The reactivity of phenyl alkyl ketone was lower than that of dialkyl ketone, and cleavage reaction was also observed. It is assumed that the cleavage products may be produced partly from the Baeyer-Villiger oxidation product because an active species in this reaction system is considered to be peroxyselenious acid, a kind of peracid.

Department of Chemical Technology
Faculty of Engineering
Osaka University
Miyakojima-ku, Osaka

Inorganic Extraction Studies on the System of Tri-n-butyl Phosphate—Nitric Acid

By Tomitaro ISHIMORI and Kenju WATANABE

(Received May 17, 1960)

Tri-*n*-butyl phosphate*, an excellent extracting agent for inorganic salts, has been widely used for the reprocessing of reactor fuel, the separation of some actinide elements from fission products and the analysis of uranium.

Results on the distribution of inorganic salts between TBP and nitric acid solution have been published by a number of investigators. Peppard et al. studied the behavior of scandium[1], yttrium[2], zirconium[1], lanthanide elements[2,3,4,5] and some actinide elements[1,3,5-7] in the extraction from nitric acid solution. McKay et al. also studied in detail the extraction of nitrates of yttrium[8], zirconium[9], lanthanide elements[8,10] and some actinide elements[11-16] with both diluted and undiluted TBP.

Distribution of uranyl[13-31] and thorium nitrate[1,7,11,15,16,20,23-25,32-39] between TBP and nitric acid solution has been studied at various concentrations of TBP, and nitric acid and/or nitrate using aluminum nitrate[18,23,25,26,33],

* Tri-*n*-butyl phosphate is abbreviated as TBP in the present paper.

1) D. F. Peppard, C. W. Mason and J. L. Maier, *J. Inorg. Nucl. Chem.*, **3**, 215 (1956).
2) D. F. Peppard, J. P. Faris, P. R. Gray and G. W. Mason, *J. Phys. Chem.*, 57, 294 (1953).
3) D. F. Peppard, W. J. Driscoll, R. J. Sironen and S. McCarty, *J. Inorg. Nucl. Chem.*, **4**, 326 (1957).
4) D. F. Peppard, P. R. Gray and M. M. Markus, *J. Am. Chem. Soc.*, **75**, 6063 (1953).
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7) D. F. Peppard, G. Asanovich, R. W. Atteberry, O. Du Temple, M. V. Gergel, A. W. Gnaedinger, G. W. Mason, V. H. Meschke, E. S. Nuchtman and I. O. Winsch, ibid., **75**, 4576 (1953).
8) D. Scargill, K. Alcock, J. M. Fletcher, E. Hesford and H. A. C. McKay, *J. Inorg. Nucl. Chem.*, **4**, 304 (1957).
9) K. Alcock, F. C. Bedford, W. H. Hardwich and H. A. C. McKay, ibid., **4**, 100 (1957).
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12) G. F. Best, H. A. C. McKay and P. R. Woodgate, ibid., **4**, 315, (1957).
13) K. Alcock, G. F. Best, E. Hesford and H. A. C. McKay, **6**, ibid., 328 (1958).
14) E. Hesford and H. A. C. McKay, *Trans. Faraday Soc.*, **54**, 573 (1958).
15) H. A. C. McKay, "Proceedings of International Conference on "Peaceful Uses of Atomic Energy, Vol. VII,P/441, United Nations Publication, New York (1956).
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sodium nitrate[15,18] or calcium nitrate[7,17] as the salting-out agent. In some cases sulfate[27,37], phosphate[27,37] or fluoride[27,33] was added in order to observe the influence of these anions on the partition of the objectives.

Distribution data for protactinium[10], neptunium[13,16,24,64] and plutonium[12,13,15,16,24,28,41,42] were also presented in the extraction with diluted TBP. According to Yakovlev and Kosyakov[43] extractabilities of americium and curium increase with the concentration of nitrate as salting-out agent in the aqueous solution. Behavior of lanthanide elements[20,23,31,35,44-49] has been often studied in the presence of uranium and/or thorium. The extraction of tetravalent cerium[48,50] from nitric acid solution with TBP was very easy in comparison with other trivalent lanthanide elements. Diluted TBP was used in order to separate zirconium from hafnium[51-53]. The extraction of fission products[23,41,42,48,54] with TBP has been evaluated for the decontamination of fissionable materials. Krieger et al.[48], who presented the extraction data of major long-lived fission products (Cs, Sr, Ru, Zr-Nb and lanthanide elements), observed that cesium was not extracted at all while strontium was extracted very slightly from a solution containing aluminum nitrate. They also mentioned that ruthenium and niobium could be extracted in a yield more than 99% into undiluted TBP. According to Bruce[54], molecular iodine was easily extracted with many diluents for TBP, but iodine extraction may have been minimized by maintaining iodine in the reduced valence state. The extractability of zirconium and niobium, given by Scadden et al.[55], from nitric acid solution containing oxalic acid into undiluted TBP was lower than that from nitric acid alone[1]. Morrison and Beaumont[20] showed that distribution ratio of molybdenum between 30% TBP-kerosene and 1 M nitric acid was 0.060 to 0.088. Diamond's observation[56] shows that molybdenum(VI) is not extracted with TBP from nitric acid. It was reported that the distribution of vanadium was very low between 25% TBP and 5 N nitric acid[57]. The distribution coefficients of ferric, cupric, nickel and chromic nitrate between TBP and nitric acid solution were given by Bartlett[18]. McKay et al[14,58,59] and Tuck[60] studied the system of TBP-diluent-nitric acid.

In this paper are presented the comprehensive and systematic studies on the distribution of ions between undiluted TBP and nitric acid of various concentration.

Experimental

The general techniques used were described in the previous paper[61]. TBP was purified in the usual way[1-3,8-13], and was used without any dilution. Nitric acid solutions were prepared by diluting concentrated chemically pure nitric acid. The acidity was determined volumetrically whenever necessary. Tracers of sodium and potassium were prepared by irradiation of the nitrates while those of manganese, nickel, germanium and tellurium were prepared from irradiated metals. A nickel tracer was separated from radiochemical impurities by an anion-exchange technique[62]. Germanium and tellurium tracers were used immediately after the separation from their daughters, respectively arsenic and iodine, by solvent extraction[63]. The imported tracers, Rb-86, Sb-124, and Os-191 were used as received. The sources of radioactive tracers other than mentioned above were the same as those shown in the previous paper[61].

The specific counting rate of these radiochemical tracers was higher than 10^4 count per min. per 100 μg. Although in some cases the oxidation state and the chemical form of the tracer could not clearly be defined, the most familiar chemical forms were chosen as far as possible. Distribution

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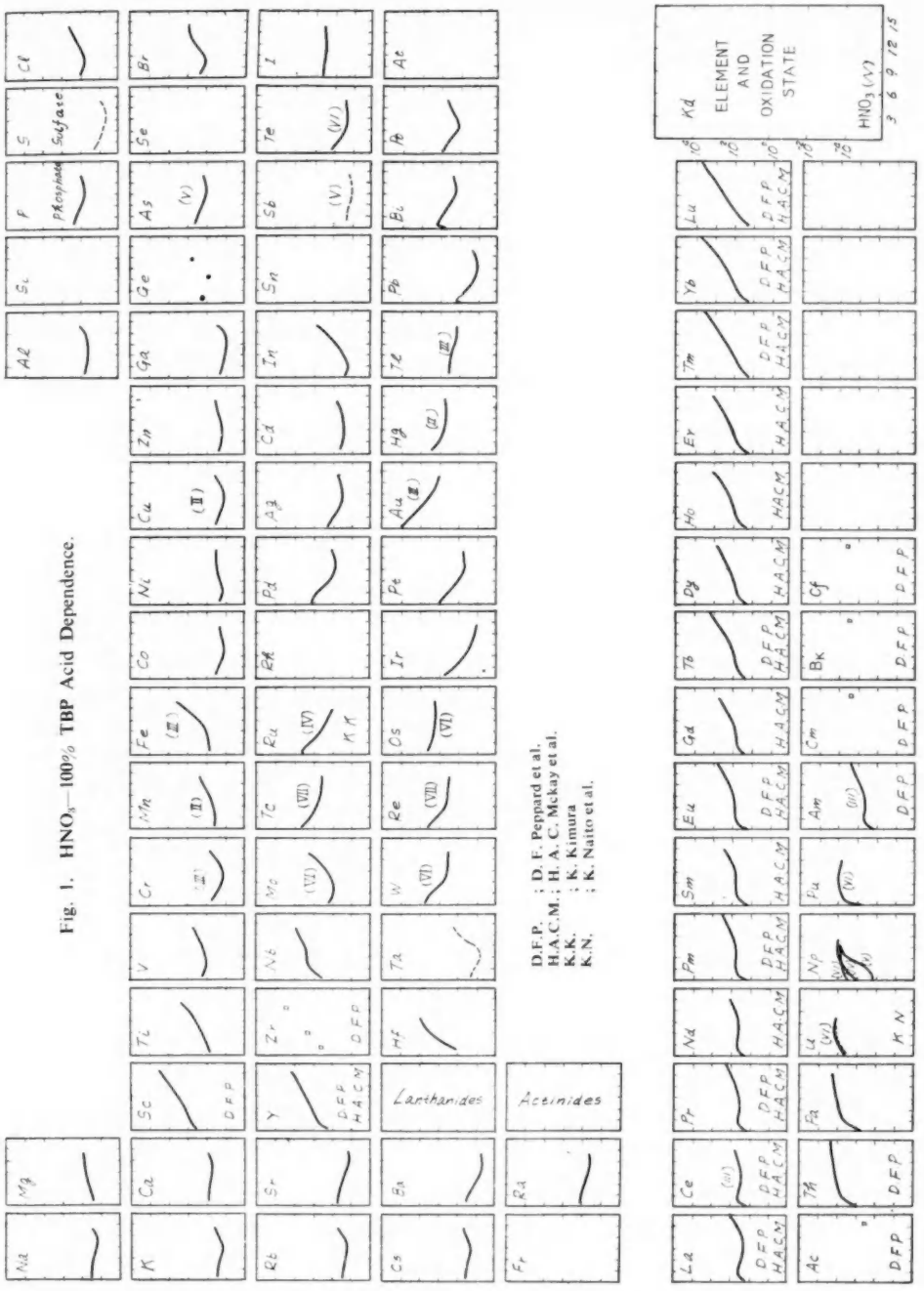


Fig. 1. HNO_3—100% TBP Acid Dependence.
D.F.P. ; D. F. Peppard et al.
H.A.C.M. ; H. A. C. Mckay et al.
K.K. ; K. Kimura
K.N. ; K. Naito et al.
Lanthanides
Actinides
ELEMENT AND OXIDATION STATE
HNO_3 (M)

ratios were determined radiometrically in the ordinary way[1,3,61,64].

Results and Discussion

The results are summarized in Fig. 1 as a series of graphs of $\log K_d$ vs. N, where K_d is the distribution ratio and N the acidity of nitric acid in normality. Some of the graphs in Fig. 1 were compiled from some published and unpublished results. Data for scandium[1], zirconium[1], thorium[1], americium[3] and some other actinide elements[5] are taken from the work of Peppard and his coworkers. Curves for yttrium[2,8] and lanthanide elements[2,5,6,10] are quoted from the reports of Peppard et al. and McKay et al. Data for ruthenium[65] and uranium(VI)[66] are cited from the observations of Kimura and Naito, respectively. A dotted line for uranium(VI) is based on the result by Bartlett[18]. The curves for hafnium, protactinum and neptunium are taken from the paper[64] of Nakamura et al. The data for plutonium(VI), lead and bismuth were obtained by one of the present authors (T. I.) during his stay in the Argonne National Laboratory, U. S. A.

The K_d values for sulfate and antimony could not be determined exactly, because the activities extracted into the organic phase were very low.

As Fig. 1 shows, four alkali elements behave in a similar way, showing always very low K_d values. There are some similarities in the shape of the acid-dependence curves for chloride and bromide; ruthenium, palladium and platinum. The K_d values of scandium, yttrium and lanthanum increase with the decreasing atomic number, Z. Calcium, strontium and barium also show a similar relationship between K_d vs. Z in a high acidity range. As far as these fifteen elements, namely, alkali metals, chloride, bromide, ruthenium, palladium, platinum, calcium, strontium, barium, scandium, yttrium and lanthanum, are concerned, there is a remarkable difference in the shape of $\log K_d$ vs. N curve between TBP-nitric and TBP-hydrochloric acid system. On the other hand, the group of alkali metals, chloride and bromide, ruthenium, palladium and platinum, calcium, strontium and barium, and scandium, yttrium and lanthanum shows a similar K_d vs. Z relationship between TBP-nitric and TBP-hydrochloric system. Among zirconium, hafnium and thorium, thorium gives the highest extractability into TBP from a nitric acid solution while it shows the lowest into TBP from a hydrochloric acid solution.

Concerning the group of zinc, cadmium and mercury, there is a marked similarity both in the shape of acid dependence curve and in values of K_d in the hydrochloric acid system[61]. In the nitric acid system, however, the K_d values of these three elements increase with atomic number, showing a noticeable difference between the shape of the acid-dependence curve for mercury and that for two other elements.

The K_d values for 12 N nitric acid were

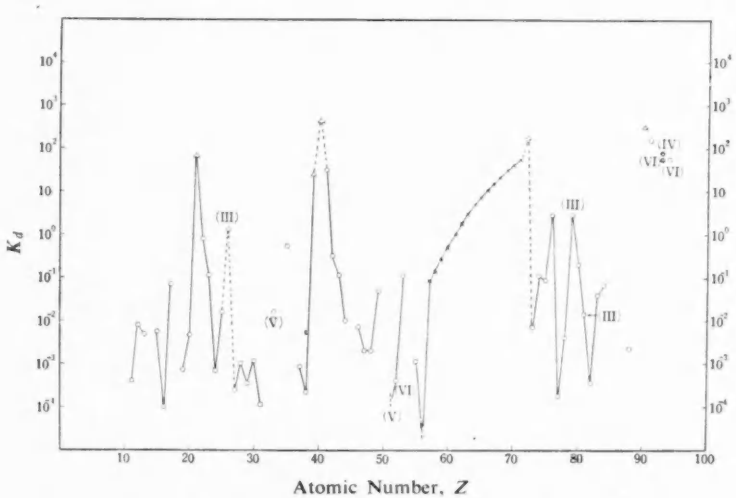


Fig. 2. Relationship between atomic number and K_d values at 12 N HNO_3.

64) T. Ishimori and E. Nakamura, This Bulletin, 32, 713 (1959).

65) K. Kimura, unpublished.

66) K. Naito et al., unpublished.

plotted against the atomic number Z, in Fig. 2. The values for lanthanides are quoted from the paper of McKay et al.[10] The values for scandium, yttrium, ruthenium and thorium are taken from both published and unpublished works[1-3,65]. There were no data for zirconium, hafnium and neptunium in 12 N nitric acid in the original papers. Accordingly the present authors indicate the values with dotted marks which are estimated from the original data. A regularity in the variation of K_d values seen in Fig. 2 is analogous to that in the TBP-hydrochloric acid system[61]. In $\log K_d$ vs. Z relationship, however, one peak for one long period of the periodic table is seen in the nitric acid system, whereas two peaks are found in the hydrochloric acid system.

Niobium and ferric nitrate give relatively high K_d values in the extraction with TBP from a concentrated nitric acid, while technetium, ruthenium, tungsten, rhenium, osmium and gold are extractable from nitric acid in low concentrations. Protactinum, uranium, neptunium(IV) and -(VI) and plutonium are extracted easily from a nitric acid solution of more than about 3 N.

Fig. 3 gives K_d values for 100% TBP-nitric acid system. This will be convenient for checking the possibility and the efficiency of a mutual separation of a couple of elements chosen arbitrarily. For example, technetium-99 will be separated with TBP from a irradiated molybdenum in 1 N nitric acid solution, because the K_d value for technetium is 18.7 in 1 N nitric acid, while that for molybdenum is 0.02.

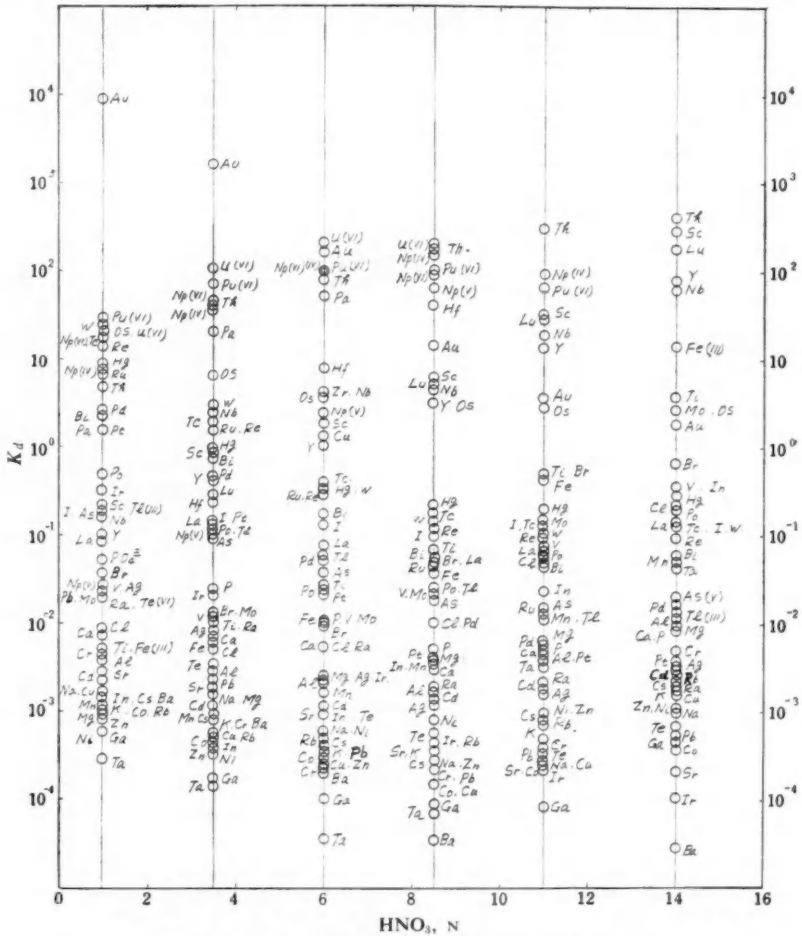


Fig. 3. K_d values in 100% TBP—HNO_3 System.

As the K_d values were obtained with a tracer in the present work, the optimum conditions of separation found in Fig. 3 will well fit a chemical separation on a tracer scale. However, some cautions must be paid in macro-scale separations.

Generally most elements give lower K_d values in the TBP-nitric acid system than in the hydrochloric acid system. In other words, it would be easy to find out a favorable condition, where many kinds of element remain in the aqueous phase after TBP extraction from nitric acid solution, while a few kinds of element are extracted into the organic phase. Accordingly, the extraction from nitric media could be applied to a chemical or a radiochemical separation not so widely as that from hydrochloric acid media could be. However, this means that a small number of elements could be isolated selectively. Isolation and group separation of scandium, yttrium, zirconium, hafnium, some actinide and lanthanide elements are promising, according to the TBP extraction data from nitric acid solution of a high acidity. Similarly, extraction from dilute nitric acid well be favorable for the isolation and group separation of technetium and ruthenium.

Chemistry Division, Tokai Laboratory
Japan Atomic Energy Research Institute
Tokai, Ibaraki-ken

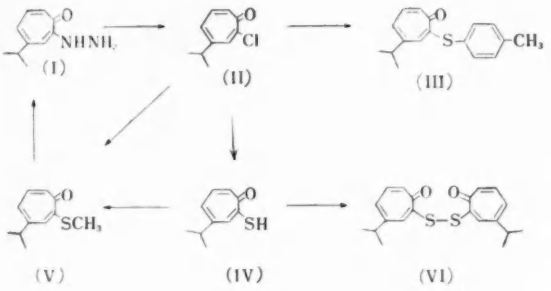
4- and 6-Isopropyl-2-mercaptotropones

By Kazuo MATSUI*

(Received April 22, 1960)

Detailed studies have been made by Nozoe and his co-workers on mercaptotropones[1-4] and mercapto derivatives of 2-phenyltropone has recently been studied by Muroi[5,6]. These studies still leave room for examination of the structure of the parent compound, 2-mercaptotropone, itself with reference to its tautomerism. As a preliminary study to this problem, homologous 4- and 6-isopropyl-2-mercaptotropones were synthesized and some reactions were carried out, which are described herein.

2-Hydrazino-4-isopropyltropone (I) and 2-hydrazino-6-isopropyltropone[7] (VII), obtained from hinokitiol (β-thujaplicin or 4-isopropyltropolone), were converted to 2-chloro-4-isopropyltropone (II) and 2-chloro-6-isopropyltropone[7] (VIII), respectively, and mercapto derivatives were prepared from them.



Scheme 1

* On leave of absence from Tokyo Research Laboratory, Tanabe Seiyaku Co., Ltd.

1) T. Nozoe, M. Sato, and K. Matsui, *Sci. Repts. Tohoku Univ.*, Series I, 37, 211 (1953).
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II easily reacted with potassium salt of *p*-thiocresol when heated in ethanol and formed 4-isopropyl-2-*p*-tolylthiotropone (III) as pale yellow plates, m. p. 110.5~112°C. Heating of II in methanol with four mol. of potassium hydrogensulfide produced 4-isopropyl-2-mercaptotropone (IV) as orange crystals, m. p. 63~65°C, in 80% yield. IV was stable in the air and the benzene layer colored dark red with ferric chloride. Methylation of IV with diazomethane in ether afforded 4-isopropyl-2-methylthiotropone (V) as a yellow oil. The identity of this compound was established by agreement of its ultraviolet spectrum with that of the product obtained by the reaction of II and potassium salt of methanethiol and admixture of their respective 2, 4-dinitrophenylhydrazone, purple needles, m. p. 183°C. Reaction of V with excess of hydrazine by refluxing in methanol for 5 hr. produced I which was identified by admixture of its benzylidene compound, yellow needles, m. p. 203°C, with that of the authentic sample.

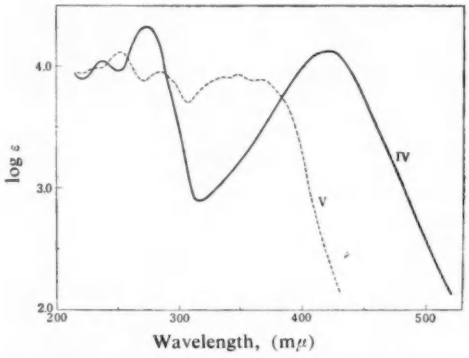
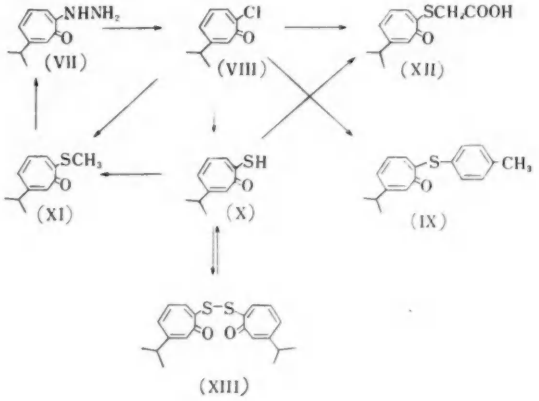


Fig. 1. Ultraviolet absorption spectra[8] of IV and V in methanol.

Application of 0.5 mol. of bromine to ethanolic solution of IV resulted in dehydrogenation from 2 mol. of IV to form 4, 4′-diisopropyl-2, 2′-ditroponyl disulfide (VI) as pale yellow cubic crystals, m. p. 155~156°C.

Heating of VIII with potassium salt of *p*-thiocresol in ethanol afforded 6-isopropyl-2-*p*-tolylthiotropone (IX) as pale yellow plates, m. p. 129~130.5°C. Similarly, application of 4 mol. of potassium hydrogensulfide gave 6-isopropyl-2-mercaptotropone (X) as dark red oil, b. $p._{.2}$ 125~130°C. X was stable in the air like IV and solely formed 6-isopropyl-2-methylthiotropone (XI) as yellow oil by the action of diazomethane. The identity of this compound was established by comparison of its ultraviolet spectrum with that of the product obtained by the reaction of VIII and potassium salt of methanethiol in ethanol and by admixture of respective 2, 4-dinitrophenylhydrazone, purple needles, m. p. 193~195°C.

Heating of XI with excess of hydrazine in methanol for 9 hr. produced VII, which was confirmed by admixture of the benzylidene compound of yellow prisms, m. p. 167°C. The formation of I from V and of VII from XI prove that in substitution reaction of halotropones with thiols, abnormal reaction seen in the case of substitution reaction with amines[9,10] does not take place.



Scheme 2

8) Measured by the Beckman Model DU spectrophotometer.

9) T. Nozoe, S. Seto and T. Sato *Proc. Japan Acad.*, **30**, 473 (1954).

10) T. Sato, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **80**, 1056 (1959).

The reaction of the sodium salt of X and sodium monochloroacetate produced 6-isopropyl-2-carboxymethylthiotropone (XII) as pale yellow prisms, m. p. 158~160°C. This compound agreed with the product obtained from the reaction of VIII and potassium thioglycolate through admixture.

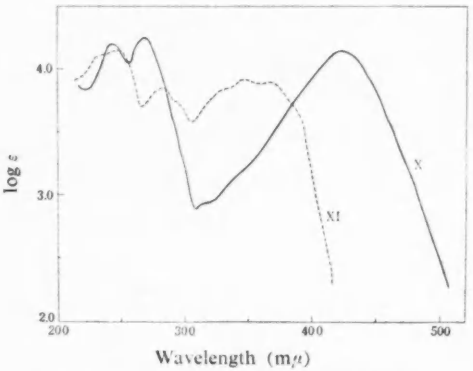


Fig. 2. Ultraviolet absorption spectra of X and XI in methanol.

Bromination of X in ethanol afforded 6, 6'-diisopropyl-2, 2-ditroponyldisulfide (XIII) as pale yellow leaflets, m. p. 210~211°C. XIII is also obtained by tosylation of X in pyridine, while heating of XIII with alkaline aqueous solution of sodium sulfide results in its reduction to form X.

There are two possible tautomeric structures, A and B, for both IV and X but this problem will be discussed in a separate report, together with that of the parent 2-mercaptotropone.

Experimental[11]

4-Isopropyl-2-*p*-tolylthiotropone (III).—A solution of 80 mg. of *p*-thiocresol, 0.5 ml. of ethanol, and 0.1 ml. of 50% potassium hydroxide was added to a solution of 0.1 g. of 2-chloro-4-isopropyltropone (II) dissolved in 0.3 ml. of ethanol and the mixture was heated on a water bath for a short time. The mixture was diluted with water and the oil that separated out was taken up in benzene. The solid obtained therefrom was recrystallized from cyclohexane to 80 mg. of III as pale yellow plates, m. p. 110.5~112°C.

Found: C, 75.22; H, 6.46. Calcd. for $C_{17}H_{19}OS$: C, 75.51; H, 6.71%[12].

11) All melting points are not corrected.

2, 4-Dinitrophenylhydrazone: Dark red prisms (from ethanol-benzene mixture), m. p. 206~207°C.

Found: C, 60.98; H, 4.73; N, 12.72. Calcd. for $C_{23}H_{22}O_4N_4S$: C, 61.32; H, 4.92; N, 12.44%.

4-Isopropyl-2-mercaptotropone (IV).—To a solution of 0.1 g. of II dissolved in 2 ml. of methanol, a solution of potassium hydrogensulfide, prepared by saturation of hydrogen sulfide in a solution of 0.26 ml. of 50% potassium hydroxide in 2 ml. of methanol, was added and the mixture was heated on a water bath for a short time. Methanol was evaporated under a reduced pressure, water was added to the residue, and the solution was treated with activated carbon. The filtrate thereby obtained was acidified with 6N sulfuric acid and the crystals that separated out were collected by filtration. Sublimation of this product under 5 mmHg pressure afforded IV as orange-red crystals m. p. 63~65°C. Yield, 80 mg.

Found: C, 66.39; H, 6.94. Calcd. for $C_{10}H_{12}OS$: C, 66.63; H, 6.71%.

Picryl derivative: Prepared from the potassium salt of IV and picryl chloride, and recrystallized from ethanol to yellow needles, m. p. 174°C.

Found: C, 49.24; H, 3.26; N, 10.88. Calcd. for $C_{16}H_{13}O_7N_3S$: C, 49.10; H, 3.35; N, 10.74%.

4-Isopropyl-2-methylthiotropone (V).—i) To a solution of 0.2 g. of II dissolved in 1 ml. of ethanol, 0.2 ml. of 50% potassium hydroxide saturated with methanethiol was added by which exothermic reaction took place. The mixture was diluted with water, extracted with benzene, and the extract was submitted to low pressure distillation, from which 0.2 g. of V was obtained as a yellow oil.

2, 4-Dinitrophenylhydrazone: Purple needles (from ethanol-benzene mixture), m. p. 183°C.

Found: C, 54.21; H, 4.62; N, 14.79. Calcd. for $C_{17}H_{18}O_4N_4S$: C, 54.53; H, 4.85; N, 14.97%.

ii) IV was methylated with diazomethane in ether by the usual process. The product thereby obtained showed good agreement with V obtained above, in ultraviolet absorption spectrum and 2, 4-dinitrophenylhydrazone.

Reaction of V and Hydrazine.—A mixture of 30 mg. of V, 0.5 ml. of methanol, and 1 drop of 80% hydrazine hydrate was refluxed for 5 hr., methanol was evaporated under a reduced pressure, and the residue was heated after addition of 2 drops of methanol and 3 drops of benzaldehyde. The crystals that separated out were collected and recrystallized from ethanol to give yellow needles, m. p. 202°C, identical with the bezylidene compound, m. p. 202°C, of 2-hydrazino-4-isopropyltropone (I).

4, 4'-Diisopropyl-2, 2'-ditroponyl Disulfide (VI).—A solution of 50 mg. of bromine in 0.5 ml. of ethanol was added to 0.1 g. of IV dissolved in 2 ml. of ethanol, by which crystals began to separate out gradually. After about 30 min. the crystals were collected and recrystallized from ethanol to give 50 mg. of VI as pale yellow, cubic crystals, m. p. 155~156°C.

Found: C, 66.96; H, 5.89. Calcd. for $C_{20}H_{22}O_2S_2$: C, 67.00; H, 6.18%.

12) The microanalyses were carried out by Miss A. Iwanaga and Mr. S. Azumi to whom the author expresses his gratitude.

6-Isopropyl-2-*p*-tolylthiotropone (IX).—A solution of 80 mg. of *p*-thiocresol, 0.1 ml. of 50% potassium hydroxide, and 0.5 ml. of ethanol was added to 0.1 g. of 2-chloro-6-isopropyltropone (VIII) in 0.3 ml. of ethanol and the mixture was heated on a water bath for a short time. This was diluted with water, crystals that separated out were collected, and recrystallized from cyclohexane to give 90 mg. of (IX) as pale yellow plates, m. p. 129～130.5°C.

Found: C, 75.19; H, 6.41. Calcd. for $C_{17}H_{18}OS$: C, 75.51; H, 6.71%.

2, 4-dinitrophenylhydrazone: Purple prisms (from ethanol-benzene mixture), m. p. 227～228°C.

Found: C, 61.03; H, 4.76; N, 12.64. Calcd. for $C_{23}H_{22}O_4N_4S$: C, 61.32; H, 4.92; N, 12.44%.

6-Isopropyl-2-mercaptotropone (X).—A solution of potassium hydrogensulfide, prepared by saturating hydrogen sulfide in a mixture of 0.46 ml. of 50% potassium hydroxide and 1.5 ml. of methanol was added to the solution of 0.18 g. of VIII dissolved in 0.5 ml. of methanol and the mixture was heated on a water bath for a short time. Methanol was evaporated under a reduced pressure, the residue was dissolved in water, and acidified with 6N sulfuric acid. The oil that separated out was taken up in chloroform and the residue from the chloroform extract was distilled under a reduced pressure, affording 0.13 g. of X as a dark red oil, b. p.$_2$ 125～130°C.

Found: C, 66.68; H, 6.48. Calcd. for $C_{10}H_{12}OS$: C, 66.63; H, 6.71%.

2, 4-dinitrophenyl derivative: Prepared from the potassium salt of X and 2, 4-dinitro-chlorobenzene and recrystallized from ethanol to give yellow prisms, m. p. 156～158°C.

Found: C, 55.17; H, 3.85; N, 8.46. Calcd. for $C_{16}H_{14}O_5N_2S$: C, 55.48; H, 4.07; 8.09%.

Picryl derivative: Prepared from the potassium salt of X and picryl chloride, and recrystallized from ethanol to give yellow needles, m. p. 145～147°C.

Found: C, 49.07; H, 3.29; N, 10.96. Calcd. for $C_{16}H_{13}O_7N_3S$: C, 49.10; H, 3.35; N, 10.74%.

6-Isopropyl-2-methylthiotropone (XI).—i) To a solution of 0.2 g. of VIII dissolved in 0.5 ml. of ethanol, 0.2 ml. of 50% potassium hydroxide saturated with methanethiol was added, by which an exothermic reaction occurred. The mixture was diluted with water, separated oil was extracted with benzene, and residue from the benzene extract was distilled under a reduced pressure, affording 0.17 g. of XI as a yellow oil.

2, 4-Dinitrophenylhydrazone: Purple needles (from ethanol), m. p. 193～195°C.

Found: C, 54.23; H, 4.48; N, 15.19. Calcd. for $C_{17}H_{18}O_4N_4S$: C, 54.53; H, 4.85; N, 14.97%.

ii) Methylation of X with diazomethane by the usual process afforded a product which was identical with the product obtained in (i) in ultraviolet absorption spectrum and 2, 4-dinitrophenylhydrazone.

Reaction of XI and Hydrazine.—A mixture of 0.1 g. of XI, 1 ml. of methanol, and 2 drops of 80% hydrazine hydrate was refluxed for 9 hr. Methanol and excess of hydrazine were removed by low pressure distillation and the residue was heated after addition of 0.5 ml. of ethanol and 5 drops of benzaldehyde. The crystals that separated out were recrystallized from ethanol to give 50 mg. of yellow prisms, m. p. 165～167°C, undepressed on admixture with the benzylidene compound, m. p. 167°C, of 2-hydrazino-6-isopropyltropone (VII).

2-Carboxymethylthio-6-isopropyltropone (XII).—(i) A solution of 60 mg. of monochloroacetic acid in 0.5 ml. of 2 N sodium hydroxide and 1 ml. of water was added to the mixture of 0.1 g. of X, 0.3 ml. of 2 N sodium hydroxide, and 1 ml. of water, and the mixture was heated on a water bath for 10 min. by which the solution changed its color from red to yellow. After treatment with activated carbon, the filtrate was acidified with 6N sulfuric acid and the crystals that separated out were collected by filtration. Recrystallization from hydrous ethanol afforded 50 mg. of XII as pale yellow prisms, m. p. 158～160°C.

Found: C, 60.88; H, 5.91. Calcd. for $C_{12}H_{14}O_3S$: C, 60.48; H, 5.92%.

ii) A solution of 50 mg. of thioglycolic acid, 0.3 ml. of 20% potassium hydroxide, and 3 ml. of ethanol was added to the solution of 90 mg. of VIII dissolved in 1 ml. of ethanol, and the mixture was heated on a water bath for 30 min. After evaporation of ethanol under a reduced pressure, water was added to the residue and the solution was treated with activated carbon. The filtrate was acidified with 6 N sulfuric acid and the crystals that precipitated out were recrystallized from hydrous ethanol to give 50 mg. of XII, m. p. 158～159°C, undepressed on admixture with the product obtained in (i).

6, 6'-Diisopropyl-2, 2'-ditroponyl Disulfide (XIII).—i) A solution of 50 mg. of bromine in 0.5 ml. of ethanol was added to the solution of 0.1g. of X dissolved in 1 ml. of ethanol, with stirring and ice-cooling. After an hour, the crystals that separated out were collected and recrystallized from benzene-ethanol mixture to give 60 mg. of XIII, as pale yellow leaflets, m. p. 210～211°C.

Found: C, 66.71; H, 6.05. Calcd. for $C_{20}H_{22}O_2S_2$: C, 67.00; 6.18%.

ii) A solution of 50 mg. of X dissolved in 0.3 ml. of pyridine was cooled with ice and 60 mg. of tosyl chloride was added to it, by which the reaction occurred with evolution of heat. The mixture was acidified with 2N hydrochloric acid and the crystals that separated out were recrystallized from a large amount of ethanol affording 30 mg. of XIII, m. p. 210～210.5°C, undepressed on admixture with the product obtained in (i).

Found: C, 67.25; H, 6.03%.

Reduction of (XIII).—A mixture of 50 mg. of XIII, 2 ml. of 2N sodium hydroxide, and 50 mg. of sodium sulfide was heated on a water bath for 10 min. by which XIII dissolved completely to form a red solution. After treatment with activated carbon, the filtrate was acidified with 6 N sulfuric acid and the oil that separated was extracted with chloroform. The residue from the chloroform extract was distilled under a reduced pressure to yield 30 mg. of X as a dark red oil, which was identified by ultraviolet absorption spectrum and the picryl derivative.

The present work was carried out while the author was a resident research chemist in the Nozoe Laboratory, Faculty of Science, Tohoku University. The author expresses his deep gratitude to Professor Tetsuo Nozoe for his kind and unfailing guidance throughout this period and to the authorities of Tanabe Seiyaku Co., Ltd. for giving him the chance to study at the above place.

Department of Chemistry
Faculty of Science,
Tohoku University
Katahira-cho, Sendai

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*Syntheses of α-, β- and γ-Dolabrins**

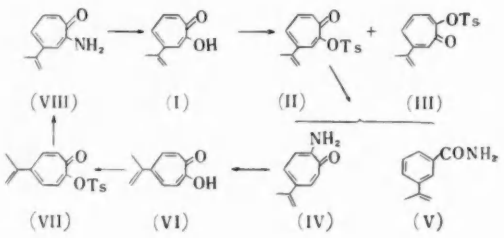
By Tetsuo Nozoe, Toshio Mukai and Toyonobu Asao

(Received April 25, 1960)

It is already known that hinokitiol (β-thujaplicin) and α-thujaplicin are present as tropolonic constituents in the essential oil of *Thujoposis dolabrata Sieb. et Zucc*[1]. Recently, the presence of β-dolabrin (4-isopropenyltropolone) in this oil was revealed in this laboratory[2], and more recently, it was also found in other species[3,4]. β-Dolabrin is the first of natural tropolones to possess a double bond in the side chain conjugated to the tropolone ring and it is interesting not only from the point of biogenesis of natural tropolones but also in the study of the chemical nature of such troponoids. For example, oxidation of β-dolabrin easily affords 4-acetyltropolone** in a high yield[2] which is an important starting material for synthesizing colchicine and its allied compounds[5].

Since there are a number of conifers containing α-, β- and γ-thujaplicines, though on different combinations according to species and habitat, there is still a possibility that α- and γ-isomers (3- and 5-isopropenyltropolones) of β-dolabrin might exist in nature[6]. In the present paper will be described the syntheses of isomeric (α-, β- and γ-) dolabrins.

According to Sato[7] in this laboratory, it is possible to convert 4-substituted tropolones to 5-substituted tropolones by utilization of the abnormal substitution of *p*-toluenesufonate of tropolones. Its reverse conversion is also possible. This reaction was applied to β-dolabrin (I). I forms two kinds of tosylates, one of m. p. 128°C and the other of m. p. 82°C, in a good yield. It is certain from the following series of experiments that the tosylate of m. p. 128°C has the structure of II and that of m. p. 82°C, the structure III. Reaction of II with methanol saturated with ammonia gives two kinds of products (IV and V), both corresponding to $C_{10}H_{10}ON$. IV turns green with ferric chloride and forms a picrate. Together with evidence of its ultraviolet spectrum (Fig. 1), IV is known to be an aminotropone derivative, while the ultraviolet spectrum of V (Fig. 1) shows it to be a benzenoid compound formed by rearrangement. Reduction of V affords *m*-cumic acid amide and, therefore, V is 3-isopropenylbenzamide. When II reacts with liquid ammonia, IV is obtained in a good yield but the rearrangement product is not



* Presented at the 11th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1958.

1) T. Nozoe, A. Yasue and K. Yamane, *Proc. Japan Acad.*, **27**, 15 (1951).

2) T. Nozoe, K. Takase and M. Ogata, *Chem. & Ind.*, **1957**, 1070.

3) J. A. F. Gardner and G. M. Barton, *Can. J. Chem.*, **36**, 1612 (1958).

4) E. Zavarin, R. M. Smith and A. B. Anderson, *J. Org. Chem.*, **24**, 1318 (1959).

** Friedel-Crafts type acylation does not occur in tropolones; Cf. Ref. 6 and P. L. Pauson, *Chem. Revs.*, **55**, 43 (1955).

5) T. Nozoe, K. Takase, J. Shin, Y. Kitahara and K. Doi, Paper presented at the 132nd Convention of the American Chemical Society, New York, September, 1957.

6) T. Nozoe, *Fortsch. Chem. org. Naturstoffe*, **13**, 232 (1956).

7) T. Sato, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 1058 (1959).

obtained. Hydrolysis of IV with alcoholic alkali gives a tropolone derivative (VI), $C_{10}H_{10}O_2$ as colorless scaly crystals, m. p. 101°C, and its reduction affords γ-thujaplicin, indicating that VI is the objective 5-isopropenyltropolone, which may be called γ-dolabrin. pK_a value of VI is 7.17 at 25°C***.

γ-Dolabrin (VI) so obtained can be led back to β-dolabrin by the same process. VI affords only one kind of tosylate (VII) whose reaction with liquid ammonia gives 2-amino-4-isopropenyltropone (VIII) and 4-isopropenylbenzamide (IX). VIII turns green with ferric chloride and is hydrolyzed in alcoholic alkali to β-dolabrin. The structure of IX was also confirmed by its reduction to *p*-cumic acid amide. Reaction of VII with methanolic ammonia gives a small amount of methyl 4-isopropenylbenzoate (X), besides VIII and IX. The ultraviolet spectra of VIII and IX are shown in Fig. 1.

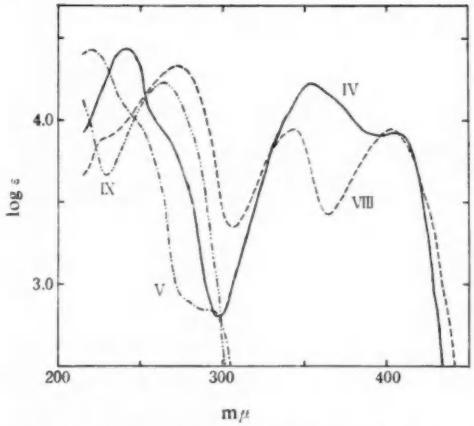


Fig. 1. Ultraviolet absorption spectra of IV, V, VIII and IX in methanol.

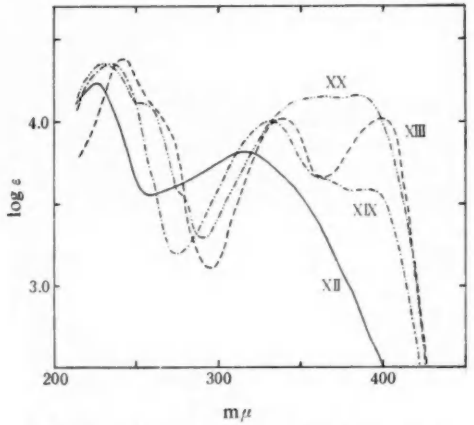


Fig. 2. Ultraviolet absorption spectra of XII, XIII, XIX and XX in methanol.

*** pK_a value was measured by Dr. N. Yui of the Institute of Applied Science, Faculty of Technology, Tohoku University, to whom the authors are deeply indebted.

Reaction of III with liquid ammonia produces an oily substance containing aminotropone and a rearrangement product, 3-isopropenylbenzamide (V). The oily substance was not induced to crystallize or led to form a crystalline derivative such as a picrate but its hydrolysis with alcoholic alkali afforded a small amount of a tropolone derivative (XI) whose copper complex was found by mixed fusion to be identical with the copper complex of α-dolabrin which will be described below. Reaction of III with methanolic ammonia afforded V but the aminotropone derivative was not isolated. The results of the amination of III show that the large steric hindrance of the 7-position to undergo abnormal substitution in III makes it difficult to be attacked by ammonia and rearrangement product V should be formed in a larger amount.

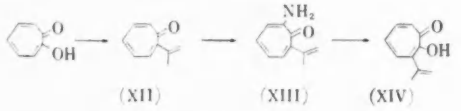
Alkaline hydrolysis of tosylate II gives β-dolabrin and rearrangement product 3-isopropenylbenzoic acid, however acidic hydrolysis of II and III gives β-dolabrin.

Tropolone is known to form the corresponding 2-alkyltropones by the action of alkyllithium or Grignard reagents[8,9] and this process was attempted for the introduction of isopropenyl group into the tropone ring. Reaction of excess of isopropenyllithium to tropolone afforded an oily substance (XII), $C_{10}H_{10}O$, whose ultraviolet spectrum (Fig. 2) indicated two absorption maxima corresponding to those of tropone[9]. Moreover, the maximum absorption of XII showed a bathochromic shift of 3 and 16 mμ respectively, from those of tropone and it seems appropriate to consider that this shift originates in the conjugation of the side chain double bond with the tropone ring. The infrared spectrum of XII supports the structure as 2-isopropenyltropone. XII is the first tropone derivative with a double bond in the side chain conjugated to the tropone ring and examination of its chemical properties appeared of interest. XII is fairly labile and increased its viscosity when left in the air. Attempted distillation at a reduced pressure resulted in resinification. XII forms an oily hydrochloride but does not produce distinct picrate or 2, 4-dinitrophenylhydrazone.

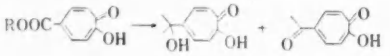
Attempted amination of XII with hydrazine[10]

8) W. von E. Doering and C. F. Hiskey, *J. Am. Chem. Soc.*, **74**, 5688 (1952).
9) T. Mukai, This Bulletin, **31**, 1547 (1958).
10) T. Nozoe, T. Mukai, J. Minegishi and T. Fujisawa, *Sci. Repts. Tohoku Univ.*, Series I, **37**, 164 (1954).

turned it black and the 2-aminotropone derivative was not isolated. Reaction of XII with hydroxylamine hydrochloride in pyridine[10] afforded the product as a brown viscous substance in the main with a trace of yellow oily substance (XIII), whose ultraviolet absorption spectrum (Fig. 2) indicated a typical curve for 2-aminotropone derivative. Hydrolysis of XIII with alcoholic alkali gave a very minute amount of a tropolone derivative (XIV), m. p. 36°C, which showed coloration with ferric chloride characteristic of tropolones and easily formed a copper complex, $C_{20}H_{18}O_4Cu$. This copper complex showed no depression of the melting point when fused with the copper complex of XI mentioned above. Paper chromatography of XI and XIV also gave spots with identical R_f value.



(XII) (XIII) (XIV)



(XVI~XVIII) (XIX) (XX)

Synthesis of γ-dolabrin was attempted by the Grignard reaction of tropolone-5-carboxylic acid alkylester. Methylmagnesium iodide was applied to tropolone-5-carboxylic acid (XV)[11], its methyl ester, and iron complex, but all these compounds were sparingly soluble in ether and the starting compound was recovered in all cases. In order to increase solubility in ether, amyl (XVI), octyl (XVII), and cyclohexyl (XVIII) esters of tropolone-5-carboxylic acid were prepared. Application of about six molar equivalents of methylmagnesium iodide against these esters afforded 5-α-hydroxyisopropyltropolone (XIX) and 5-acetyltropolon (XX). The ultraviolet absorption spectra of XIX and XX are indicated in Fig. 2. The structure of XIX was confirmed from the fact that dehydration of XIX by heating with potassium hydrogensulfate easily afforded γ-dolabrin (VI). XIX turns green in aqueous layer to ferric chloride but the color does not transfer to benzene or chloroform layer. This is the general behavior of hydroxyl or carboxyl derivatives of tropolone. XIX is easily dehydrated and changes partly into VI on heating with acid or by sublimation. 5-Acetyltropolone (XX) is also obtained by oxidation of VI. XX easily forms an oxime, the same as 4-acetyltropolone as already reported[5], and also undergoes condensation with benzaldehyde derivatives to

11) Y. Kitahara, ibid., 40, 74 (1956).

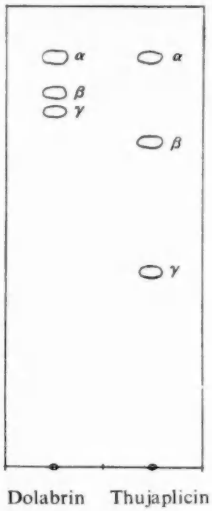


Fig. 3. Paper chromatogram of α-, β- and γ-dolabrin and α-, β- and γ-thujaplicin.

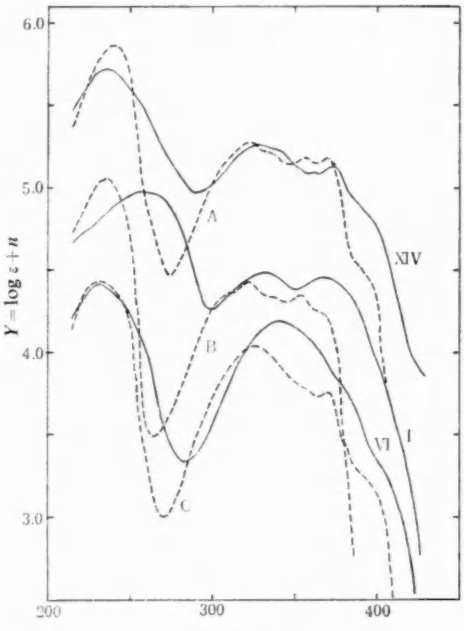


Fig. 4. Ultraviolet absorption spectra of α-, β- and γ-dolabrin (XIV, I and VI), and α-, β- and γ-thujaplicin (A, B and C).

$Y = \log + 1.5$ (for α-series)
$Y = \log + 0.7$ (for β-series)
$Y = \log + 0$ (for γ-series)

form 5-cinnamoyltropolone derivatives.

The work described in this paper has completed the total syntheses of α-, β- and γ-dolabrins, and 4-, and 5-acetyltropolones.

The paper chromatogram**** of α-, β- and γ-dolabrins so obtained is shown in Fig. 3, and their ultraviolet absorption spectra, together with those of corresponding thujaplicins are given in Fig. 4. The spectra of dolabrins show a bathochromic shift from those of corresponding thujaplicins, due to conjugation of the isopropenyl group with the tropolone ring. The absorption of γ-dolabrin in the longer wavelength region differs from that of α- and β-isomers.

Experimental[12]

***p*-Toluenesulfonate (II and III) of β-Dolabrin (I).**—To a solution of 1 g. of β-dolabrin dissolved in 1.5 ml. of pyridine, 1.4 g. of *p*-toluenesulfonyl chloride was added and the mixture was allowed to stand for about 1 hr. The colorless needles that precipitated out by addition of 4 ml. of ethanol were collected by filtration. Recrystallization of crude crystals, m. p. 124~126°C, from ethanol afforded 820 mg. of II as colorless plates, m. p. 127~128°C. Ethanol was evaporated from the filtrate left after removal of II, water was added to the residue, and the solution was extracted with benzene. The benzene extract was dried, passed through a chromatographic column of alumina, and eluted with benzene. 850 mg. of crystals, m.p. 72~74°C, thereby obtained were recrystallized from ethanol to III as pale yellow scales, m. p. 81~82°C.

Found (for II): C, 64.67; H, 4.66. Found (for III): C, 64.64; H, 4.96. Calcd. for $C_{17}H_{16}O_4S$: C, 64.55; H, 5.10%.

Reaction of 2-Tosyloxy-4-isopropenyltropone (II) and Ammonia a) A solution of 300 mg. of II dissolved in 30 ml. of methanol saturated with ammonia was allowed to stand at room temperature for 4 days. Methanol was evaporated under reduced pressure and the residue was treated with benzene, from which 165 mg. of ammonium *p*-toluenesulfonate was obtained as the insoluble portion. The benzene soluble portion was chromatographed over alumina and eluted with benzene, affording 70 mg. of yellow crystals m. p. 99~102°C. Subsequent elution with ethyl acetate gave 30 mg. of crystals, m. p. 119~123°C. Recrystallization of the former from benzene-cyclohexane mixture afforded IV as yellow needles, m. p. 110~112°C, while that of the latter from benzene-cyclohexane gave V as colorless scales, m. p. 126~126.5°C.

Found (for IV): C, 74.34; H, 6.90; N, 8.09. Found (for V): C, 74.29; H, 6.93; N, 8.75. Calcd. for $C_{10}H_{11}ON$: C, 74.51; H, 6.88; N, 8.69%.

IV forms a picrate of yellow prisms, m. p. 174~175°C (decomp.).

Found: C, 48.80; H, 3.26; N, 14.42. Calcd. for $C_{16}H_{14}O_8N_4$: C, 49.23; H, 3.62; N, 14.36%.

b) A mixture of 200 mg. of II and 13 ml. of liquid ammonia was allowed to stand at room temperature for 2 days and ammonia was evaporated. The residue was extracted with benzene and 60 mg. of IV was obtained. Purification of its filtrate by chromatography afforded 30 mg. of IV but none of V.

γ-Dolabrin (VI) from 2-Amino-5-isopropenyltropone (IV).—A mixture of 200 mg. of IV and 500 mg. of sodium hydroxide in 3 ml. of 30% ethanol was refluxed. The yellow crystals that precipitated out were collected, dissolved in water, and the solution was neutralized with 2 N hydrochloric acid, from which 150 mg. of colorless crystals, m. p. 94~96°C, was obtained. Recrystallization from benzene-cyclohexane mixture afforded VI as colorless scales, m. p. 100~101°C.

Found: C, 73.72; H, 5.86. Calcd. for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22%.

I. R. Spectrum: $\tilde{\nu}$ (O-H, C=O, C=C) 3215, 1606, 1595, δ (=CH_2) 907 cm^{-1}. (in KBr disk).

Copper complex: Green needles, m. p. over 290°C.

Found: C, 62.02; H, 4.49. Calcd. for $C_{20}H_{18}O_4Cu$: C, 62.24; H, 4.70%.

Reduction of γ-Dolabrin (VI) and 3-Isopropenylbenzamide (V).—a) A solution of 20 mg. of VI dissolved in 4 ml. of ethanol, added with 5 mg. of palladium-carbon, was submitted to hydrogenation and 3 ml. of hydrogen was absorbed. Ethanol was evaporated and the crystalline residue was sublimed under reduced pressure. Recrystallization of the sublimate from cyclohexane afforded colorless needles, m. p. 77~78°C, which showed no depression on admixture with γ-thujaplicin, m. p. 80°C.

b) Fifteen mg. of V was hydrogenated by the same way as above to afford 7 mg. of colorless scales, m. p. 94~95°C after recrystallization from benzene-cyclohexane, which showed no depression on admixture with *m*-cumic acid amide m. p. 95~95.5°C.

***p*-Toluenesulfonate (VII) of γ-Dolabrin (VI),**—To a solution of 260 mg. of γ-dolabrin dissolved in 0.5 ml. of pyridine, 360 mg. of *p*-toluenesulfonyl chloride was added and the mixture was allowed to stand. After about 1.5 hr. 2 ml. of ethanol was added to it and 410 mg. of crystals m. p. 121~124°C was obtained. The filtrate was evaported and the residue was poured into water, separating 70 mg. of crystals m. p. 119~124°C. The combined crystals were recrystallized from ethanol to VII as pale yellow prisms, m. p. 125~126°C.

Found: C, 64.74; H, 5.04. Calcd. for $C_{17}H_{16}O_4S$: C, 64.55; H, 5.10%.

Reaction of 2-Tosyloxy-5-isopropenyltropone (VII) and Ammonia.—a) A mixture of 320 mg. of VII dissolved in 15 ml. of liquid ammonia was allowed to stand for 5 days at room temperature,

**** Chromatography is carried out on the paper treated with 17% aqueous solution of phosphoric acid, and benzene used as developing solvent.

12) M. p.'s are uncorrected. The microanalyses were carried out by Messrs Shin-ichi Ohyama, Kazuyoshi Azumi and Miss Ayako Iwanaga, and infrared spectra were measured with Perkin-Elmer Model 21 double beam spectrophotometer by the member of Prof. Kinumaki's laboratory of the Chemical Research Institute of Non-aqueous solutions, to whom the authors' acknowledgements are hereby extended.

then ammonia was evaporated, and the residue was extracted with benzene. The benzene solution was passed through an alumina layer. The first elution with benzene-ethyl acetate afforded 100 mg. of yellow crystals, m. p. 90~97°C, and subsequent elution with ethyl acetate afforded 30 mg. of colorless crystals, m. p. 181°C. Recrystallization of the former from benzene-petroleum ether afforded VIII as yellow needles, m. p. 100~101°C. The latter was recrystallized from a mixture of ethyl acetate and petroleum ether, affording IX as colorless plates, m. p. 180.5~182°C. Catalytic reduction of IX with polladium-carbon afforded colorless crystals, m. p. 152°C, which showed no depression on admixture with *p*-cumic acid amide, m. p. 153°C.

Found (for VIII): C, 74.17; H, 6.41; N, 8.92. Found (for IX): C, 74.33; H, 6.62; N, 8.62. Calcd. for $C_{10}H_{11}ON$: C, 74.51; H, 6.88; N, 8.69%.

Picrate of VIII: m. p. 130~131°C.

Found: C, 49.72; H, 3.48; N, 14.41. Calcd. for $C_{16}H_{14}O_7N_4$: C, 49.23; H, 3.62; N, 14.36%.

b) A solution of 400 mg. of VII dissolved in 50 ml. of methanol saturated with ammonia was allowed to stand for 4 days at room tepmerature and then the methanol was evaporated. The residue was extracted with benzene, and the benzene-insoluble portion was extracted with water. The insoluble residue was 100 mg. of crystals melting at 180°C. The sparingly soluble portion of benzene extract afforded 30 mg. of the same crystals. Both lots of crystals corresponded to IX. The benzene-soluble portion was chromatographed over alumina and elution with benzene gave 5 mg. of crystals X, m. p. 50~53°C, which showed no depresseon on admixture with methyl *p*-isopropenylbenzoate. The portion eluted with ethyl acetate affored 15 mg. of *β*-dolabrin, m.p. 51°C, by the same hydrolysis as below.

Hydrolysis of 2-Amino-4-isopropenyltropone (VIII).—A solution of 30 mg. of VIII dissolved in a mixture of 150 mg. of potassium hydroxide, and 1 ml. of 50% methanol was refluxed for 3.5 hr. The methanol was then evaporated, 2 ml. of water was added to the residue, and this was extracted with benzene to remove an unreacted substance, the mother liquor was acidified, extracted with benzene, and benzene was evaporated after drying. Recrystallization of its residue from cyclohexane afforded 23 mg. of pale yellow needles, m. p. 54~56°C, which showed no depression on admixture with *β*-dolabrin

Reaction of 2-Tosyloxy-6-isopropenyltropone (III) and Ammonia.—a) A mixture of 2 g. of III and about 20 ml. of liquid ammonia was allowed to stand for 2 days at room temperature. The ammonia was evaporated and the residue was extracted with benzene. The benzene solution was washed with water, dried, and chromatographed over alumina. Elution with benzene afforded 490 mg. of yellow oil (A), and subsequent elution with ethyl acetate afforded 220 mg. of (V), m. p. 124°C. A was refluxed with a mixture of 1 g. of potassium hydroxide, and 5 ml. of 50% ethanol for 8 hr. Ethanol was then evaporated, 5 ml. of water was added to the residue, and this was extracted with benzene. Mother liquor was acidified and extracted with benzene, affording a minute quantity of oil (XI), and this was derived to a copper complex by reaction with copper sulfate solution and 50 mg. of green crystals was obtained. Recrystallization from chloroform-petroleum ether afforded greenish yellow needles, m. p. 250°C (decomp.).

b) A solution of 2 g. of III dissolved in 200 ml. of methanol saturated with ammonia was allowed to stand for 3 days at room temperature and the solvent was evaporated. The residue was dissolved in benzene and 220 mg. of V m. p. 124°C was obtained. The filtrate was evaporated and the residue was refluxed for 2 hr. with a solution of 1 g. of sodium hydroxide in 5 ml. of 50% ethanol. The colorless needles, $C_{10}H_{13}O_2N$, m. p. 179.5~180.5°C (after recrystallization from benzene) were obtained by neutralization of the solution. However, the structure of this acidic substance was not defined.

Found (for m. p. 179.5°C): C, 66.97; H, 7.11; N, 7.73. Calcd. for $C_{10}H_{13}O_2N$: C, 67.02; H, 7.31; N, 7.82%.

Synthesis of 2-Isopropenyltropone (XII) from Tropolone.—A solution of 6.4 g. (0.053 mol. eq.) of 2-bromopropene dissolved in 10 ml. of ether was added dropwise into 0.65 g. (0.093 mol. eq.) of lithium in 12 ml. of ether with stirring in nitrogen atmosphere and the mixture was refluxed for 2 hr. After removal of residual lithium pieces, a solution of 1.15 g. (0.0093 mol. eq.) of tropolone dissolved in 50 ml. of ether was added dropwise with stirring and the mixture was stirred for 1 hr. The solution was cooled with ice and 20 ml. of 2 N sulfuric acid was added, the ether layer was separated, and the aqueous layer was extracted with ether. The combined ether solution was washed with sodium chloride solution, passed through an alumina layer to remove unreacted tropolone, and the ether was evaporated from the effluent, leaving 1.5 g. of pale reddish brown oil. Bromination of this oil in glacial acetic acid failed to produce any crystalline derivative. The oil was dissolved in benzene and dry hydrogen chloride gas was passed through this solution. The oily hydrochloride that separated out was collected, decomposed with water, and extracted with ether. The ether extract was washed with water, dried, and passed through a column of alumina. Evaporation of ether from the effluent afforded a reddish brown oil, n_D^{25} 1.6978, which was submitted to elemental analyses and spectral measurement.

Found: C, 81.33; H, 7.01. Calcd. for $C_{10}H_{10}O$: C, 82.16; H, 6.90%.

I. R. spectrum: $\tilde{\nu}$ (C=O, C=C) 1627, 1570~1600, δ (=CH_2) 897 cm^{-1} (in KBr disk).

Reaction of 2-Isopropenyltropone and Hydroxylamine: (Synthesis of *α*-Dolabrin (XIV)).—A solution of 0.2 g. of 2-isopropenyltropone and 0.3 g. of hydroxylamine hydrochloride dissolved in a mixture of 1.5 ml. of dehydrated ethanol and 1.5 ml. of pyridine was refluxed for 2 hr. Ethanol was then evaporated, water was added to the residue, and the solution was extracted with benzene. The benzene extract was washed with water and passed through an alumina layer. First elution with benzene

afforded 20 mg. of red oil (A) and subsequent elution with chloroform and ethanol respectively afforded 10 mg. of yellowish oil (B) and 50 mg. of yellowish brown oil (C). A part of A underwent crystallization but was not purified and it was assumed to be an oxime from its ultraviolet spectrum. λ_{max}^{MeOH} mμ (log ε): 223 (4.17), 299 (3.71), 390~400 (3.11).

B also afforded no crystalline picrate but it was assumed from its ultraviolet spectrum to be 2-aminotropone derivative.

It was considered possible that C contains a 2-aminotropone derivative. Therefore, it was refluxed for 2 hr. with 0.2 g. of sodium hydroxide and 2 ml. of 50% ethanol, the ethanol was evaporated, water was added to the residue, and the solution was extracted with chloroform to remove the neutral portion. The aqueous layer was acidified and extracted with chloroform, affording 20 mg. of a brown oil. Distillation of this oil under a reduced pressure gave pale yellow crystals, m. p. 35~36°C, which was dissolved in petroleum ether and derived to a copper complex. The copper comprex came as greenish yellow crystals, m. p. 250°C (decomp.).

Found: C, 61.56; H, 5.15; Cu, 16.29. Calcd. for $C_{20}H_{18}O_4Cu$: C, 62.24; H, 4.70; Cu, 16.46%.

Synthesis of Esters of Tropolone-5-carboxylic Acid (XV).—*a) Amyl Ester (XVI).*—To a solution of 600 mg. XV dissolved in 10 ml. of amyl alcohol, 0.15 ml. of conc. sulfuric acid was added and the mixture was refluxed for 2 hr. The solution was filtered to remove carbonized material, the filtrate was concentrated, and the residue was allowed to stand with the addition of ethanol. The residue afforded 450 mg. of crystals melting at 60°C which was recrystallized from petroleum ether to XVI as colorless, scales m. p. 61~62°C. This substance turns red with ferric chloride and the color transfers to the chloroform layer.

Found: C, 66.30; H, 6.74. Calcd. for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83%.

Hydrolysis of this mother liquor with alkali resulted in recovery of 150 mg. of XV, m. p. over 250°C.

b) Octyl Ester (XVII).—Obtained by the same method as a) as colorless scales, m. p. 55°C.

Found: C, 69.53; H, 8.12. Calcd. for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97%.

c) Cyclohexyl Ester (XVIII).—To a solution of 600 mg. of XV dissolved in 12 ml. of cyclohexanol, 0.6 ml. of conc. hydrochloric acid was added and the mixture was refluxed for 8 hr. The reaction mixture was filtered while hot, the filtrate was concentrated, and allowed to stand. Evaporation was repeated twice and 800 mg. of crystals of m. p. 85°C was obtained as the first crop, and 140 mg. of crystals of m. p. 90°C as the second crop. The combined crystals were recrystallized from ethanol and 60 mg. of tropolone-5-carboxylic acid, m. p. over 250°C, was obtained from the sparingly soluble portion, and 600 mg. of pale brown plates XVIII, m. p. 94~95°C, from the easily soluble portion. Further recrystallization of the latter raised its melting point to 97~98°C.

Found: C, 67.07; H, 6.23. Calcd. for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50%.

Synthesis of γ-Dolabrin (VI) from the Esters of Tropolone-5-caboxylic Acid.—a) A solution of 0.5 g. (0.0017 mol. eq.) of XVII dissolved in 10 ml. of ether was added with stirring under ice-cooling to the Grignard reagent from 1.6 g. (0.0113 mol. eq.) of methyl iodide, 0.26 g. (0.0104 mol. eq.) of magnesium, and ether, and the mixture was stirred for 3 hr. Ten ml. of 15% ammonium chloride solution was added to this mixture and the whole mixture was extracted thoroughly with ether. The ether was evaporated, the residue was heated with 10 ml. of 6 N sulfuric acid for 10 min. and the mixture, was extracted with three 5-ml. portions of chloroform, affording 250 mg. of dark brown oil A. The mother liquor left after chloroform extraction was extracted with eight 5-ml. portions of ethyl acetate, affording 40 mg. of pale yellow oil (B). A part of B crystallized on being allowed to stand, but its melting point could not be measured. B was submitted to paper chromatography with benzene as a solvent but it did not move with this solvent. A mixture of B and finely divided fused hydrogensulfate was heated for a few minutes at 140°C and the mixture was sublimed under reduced pressure, from which 20 mg. of colorless crystals, m. p. 90~95°C, was obtained. Recrystallization from cyclohexane afforded colorless plates, m. p. 99~100°C, undepressed on admixture with γ-dolabrin. This has indicated that B chiefly contains the objective 5-α-hydroxy-isopropyltropolone (XIX). Some crystals separated out on standing A and 25 mg. of pale yellow crystals, m. p. 178°C, was obtained. It showed no depression of the melting point on admixture with 5-acetyltropolone (XX). The mother liquor left after separation of these crystals was found to contain the octyl ester, XIX, and XX.

b) Reaction of 0.42 g. of the amyl ester (XVI) with 6 molar equivalents of methylmagnesium iodide, as in the case of the above a), was carried out. After completion of the reaction, the product was decomposed with 15 ml. of 6 N sulfuric acid. After separation of the ether layer, the mother liquor was extracted with 20 ml. and 10 ml. of chlololform, and the combined ether and chloroform extracts were washed with eight 10-ml. portions of 8 N sulfuric acid. Evaporation of the solvent from this combined extract left 250 mg. of oil A. Sulfuric acid layer and washings were combined, neutralized to pH 4 with dil. potassium hydroxide solution, and the solution continuously extracted with chloroform for 10 hr. Evaporation of chloroform from this extract afforded 80 mg. of oil which underwent crystallization. The crystals were washed out repeatedly with cyclohexane, the cyclohexane was evaporated, and the residue was sublimed under reduced pressure, affording 40 mg. of pale yellow crystals, m. p. 98~99°C, undepressed on admixture with γ-dolabrin (VI). Paper chromatographic examination showed A to be a mixture of the recovered ester, XIX, and XX.

c) A solution of 0.42 g. of the cyclohexyl ester (XVIII) dissolved in 12 ml. of ether was reacted with 6 molar equivalents of methylmagnesium iodide as in the case of (a), stirring for 1 hr. and

refluxed for 30 min. After it was cooled, 15 ml. of 4 N sulfuric acid was added to effect decomposition, extracted with ether, and the ether was evaporated after washing with water and drying over sodium sulfate, affording 250 mg. of yellow oil (A). The sulfuric acid layer was extracted 5 times with 5 ml. of chloroform each time, and the extract was washed with water, dried, and evaporated, to leave 50 mg. of oil. This crystallized immediately and was found to contain chiefly XIX and a small amount of XX. This substance actually gave green coloration in the aqueous layer and pale reddish brown coloration in the chloroform layer with ferric chloride. There was no suitable solvent for recrystallization of the above crystals but on leaving its ethalolic solution, comparatively large plate crystals, m. p. 101~104°C, separated out on the wall of the vessel. A chromatographic test indicated that A contained the recovered ester, XIX, and XX. Crystals separated out on standing A and 15 mg. of XX, m. p. 178~180°C, was obtained. The benzene solution of filtrate was chromatographed over silica gel but it was not successfully separated into its components.

5-Acetyltropolone (XX) from γ-Dolabrin (VI).—A solution of 770 mg. of VI dissolved in 27 ml. of formic acid, to which was added 6 ml. of 35% hydrogen peroxide, was stirred at 40°C for 3 hr. and formic acid was distilled off under reduced pressure. Further 7 ml. of 1.2 N sodium hydroxide was added and the mixture was stirred at 40°C for 3 hr. This was acidified with 2 N hydrochloric acid and extracted with chloroform. The aqueous layer was cooled with ice, an aqueous solution of 900 mg. of periodic acid dihydrate was added, mixture was stirred, and 590 mg. of crystals was obtained. The same amount of crystals, 70 mg., was obtained from the chloroform layer. The combined crystals were recrystallized from ethanol to XX as yellow plates, m. p. 182~183°C.

Found: C, 65.69; H, 4.49. Calcd. for $C_9H_8O_3$: C, 65.85; H, 4.91%.

Oxime: Pale yellow plates, m. p. 201~202°C (decomp.).

Found: C, 60.55; H, 4.75; N, 7.81. Calcd. for $C_9H_9O_3N$: C, 60.33; H, 5.00; N, 7.82%.

Condensation of XX with Benzaldehyde and 3, 4, 5-Trimethoxybenzaldehyde.—a) A mixture of 650 mg. of XX suspended in 10 ml. of methanol to which was added 700 mg. of benzaldehyde, 1.3 ml. of 5% potassium hydroxide solution, and 15 ml. of water was stirred thoroughly and the orange crystals that separated out were collected by filtration. This substance was dissolved in 100 ml. of water, acidified with 2 N hydrochloric acid, and 900 mg. of yellow needles was recrystallized from ethanol to yellow needles, m. p. 158~159°C.

Found: C, 76.04; H, 4.32. Calcd. for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80%.

b) A mixture of 100 mg. of XX and 150 mg. of trimethoxybenzaldehyde afforded 150 mg. of a condensate of m. p. 207.5~208.5°C after recrystallization from acetic acid.

Found: C, 66.16; H, 5.12. Calcd. for $C_{19}H_{18}O_6$: C, 66.66; H, 5.30%.

The authors gratefully acknowledge financial help for part of the expenses for the present work from the Ministry of Education by a Grant-in-Aid for Scientific Research and from the Sankyo Co., Ltd., and the donation of samples from the Takasago Perfumery Co., Ltd. The writers are indepted to Mr. Yasuo Toyooka for technical assistance.

Department of Chemistry
Faculty of Science
Tohoku University
Katahira-cho, Sendai

Infrared Spectra of p-Bromophenacyl Esters

By Hisao NAKATA, Shuzo MATSUO* and Yoshimasa HIRATA

(Received January 6, 1960)

In previous papers[1,2] it has been demonstrated that aureothinic acid and *N*-benzoyl aminotetrahydroaureothinic acid have structures (I) and (II), respectively. The location of an etheric oxygen at an α-position of the carboxyl group in these acids was suggested by the comparison of infrared spectra of several model compounds[1] and was established rigorously by oxidative studies[2].

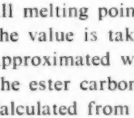
During the course of the structural elucidation of these acids, however, attention was called to the fact that the infrared spectra of their *p*-bromophenacyl esters in chloroform solution show ester carbonyl absorption at

* Institute of Chemical Research, Nippon Shin-yaku Co. Ltd., Nishioji, Hachi-jo, Minami-ku, Kyoto.

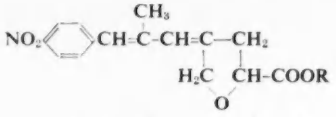
1) H. Nakata, Y. Hirata, K. Okuhara, K. Yamada, T. Naito and K. Iwadare, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 379 (1958).

2) Y. Hirata, H. Nakata and K. Yamada, ibid., **79**, 390 (1958).

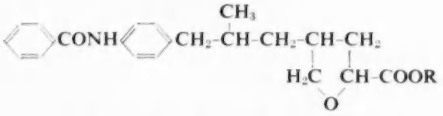
TABLE I. INFRARED SPECTRA OF *p*-BROMOPHENACYL ESTERS ($RCOOCH_2COC_6H_4Br$-*p*) IN CHLOROFORM SOLUTION

No.	Compound R-	m. p.[a] °C	Ester C=O cm^{-1}	Keto C=O cm^{-1}	$\sum(\sigma^*)$[b]
1	n-C_7H_{15}-	65～66	1743	1707	−0.130[c]
2	n-C_5H_{11}-	71～72	1742	1707	−0.130[c]
3	n-C_3H_7-	62～63	1743	1707	−0.115
4	C_2H_5-	55～58	1743	1705	−0.100
5	CH_3-	75～78	1744	1703	0.000
6	$C_6H_5CH_2$-	84～86	1748	1708	+0.215
7	$CH_3OCOCH_2CH_2$-[d]	105～106	1746	1708	+0.254[e]
8	$CH_3CHClCH_2$-	75～76	1749	1708	+0.270[f]
9	$CH_3CH(OH)$-	111～112	1750	1708	+0.455[f]
10	H-	100～101[g]	1737	1706	+0.490
11	$C_2H_5OCH_2$-	106～107	1763	1706	+0.520
12	n-$C_4H_9OCH_2$-	90～91	1764	1706	+0.520
13	$HOCH_2$-	136～138	1751	1707	+0.555
14	$C_6H_5CONHCH_2$-[h]	148～149	1753	1706	+0.727[i]
15	$C_6H_5CH(OH)$-	113～114	1750	1707	+0.765
16	$C_6H_5OCH_2$-	149～150	1774	1707	+0.850
17	ICH_2-	99～100	1751	1710	+0.850
18	CH_3CH_2CHBr-	(oil)	1753	1712	+0.885[f]
19	$(C_6H_5)_2C(OH)$-	154～155	1743	1710	+0.960[f]
20	$ClCH_2$-	105～106	1756	1705	+1.050
21	Aureothinic acid (Ia)	174～175	1758	1706	+0.390[f]
22	*N*-Benzoyl aminotetrahydroaureothinic acid (IIa)[j]	145～146	1758	1707	+0.390[f]
23	$CH_3COCH(CH_3)CH_2$-[k]	91	1745	1698	+0.099[f]
24		105～106	1751	1702	+0.720[m]

a) All melting points are uncorrected.
b) The value is taken from Taft (Refs. 3 and 4), unless otherwise indicated.
c) Approximated with the value for n-C_4H_9- substituent.
d) The ester carbonyl group appeared at 1738 cm^{-1}.
e) Calculated from the value for CH_3OCO- substituent using the inductive parameter of 2.8 (Refs. 3 and 4).
f) Calculated using the additive nature of σ^* values (Refs. 3 and 4).
g) T. Kubota and T. Matsuura, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **72**, 482 (1951).
h) The amide carbonyl group appeared at 1663 cm^{-1}.
i) Estimated from the relations $\sigma^*=\sigma_I/0.45$ and $\sigma_I=(\alpha\cdot\sigma_p-\sigma_m)/(\alpha-1)$ (Refs. 3 and 4, and R. W. Taft, Jr. and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958).), using σ_p of +0.078 and σ_m of +0.217 (H. H. Jaffe, *Chem. Revs.*, **53**, 191 (1953).) and $\alpha=+0.443$ (J. L. Roberts and H. H. Jaffe, *J. Am. Chem. Soc.*, **81**, 1635 (1959).).
j) The amide carbonyl group appeared at 1660 cm^{-1}.
k) R. B. Bradbury and S. Masamune, *J. Am. Chem. Soc.*, **81**, 5201 (1959).
l) The lactone carbonyl group appeared at 1779 cm^{-1}.
m) The σ^* value for CH_3COOCH_2- group was estimated as +1.010 from the same relations cited in foot-note i) of this Table using σ_p of +0.31 and σ_m of +0.39 (D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).), and $\alpha=+0.448$ (J. L. Roberts and H. H. Jaffe, *J. Am. Chem. Soc.*, **81**, 1635 (1959).). The additive nature of σ^* values then leads to the value of +0.720 for this γ-lactone grouping.



(I) R=H, aureothinic acid
(Ia) R=$CH_2COC_6H_4Br$-*p*



(II) R=H, *N*-benzoyl aminotetrahydro-aureothinic acid
(IIa) R=$CH_2COC_6H_4Br$-*p*

1758 cm^{-1}, which is considered to be an abnormally high frequency, and it became desirable to examine the infrared spectra of several *p*-bromophenacyl esters. Consequently, twenty *p*-bromophenacyl esters were prepared and their spectra were measured in chloroform solution. The results are summarized in Table I.

The absorption bands of keto carbonyl groups appear in the same frequency range of 1705~1710 cm^{-1}. On the other hand, in the spectra of the ester carbonyl groups an etheric function located at an α-position of the carboxyl group causes a considerable shift of frequency, as is evident from Table I (compounds No. 11, 12, 16, 21 and 22). While the inductive effect of electronegative α-oxygen substituents has usually been cited as the probable cause for the frequency shifts, it has not been possible to differentiate this from direct field effects. A more quantitative understanding of these may be discussed in terms of inductive parameters of the substituents. When the polar substituent constant σ^* reported by Taft[3,4] is taken as a measure of inductive effects, the ester carbonyl frequencies presented in Table I define a straight line when plotted against the appropriate σ^*-values (Fig. 1). The linear correlation obtained is reasonably good and it was found possible to write the following approximate relation:

$$\nu_{C=O}\ cm^{-1} = 1745\ cm^{-1} + 9.1(\Sigma\sigma^*)cm^{-1} \qquad (1)$$

It is apparent from Fig. 1 that the absorption bands of both aureothinic (No. 21) and *N*-benzoyl aminotetrahydroaureothinic (No. 22) esters deviate from the correlation line by an amount of 10 cm^{-1}. The deviations are more serious with the ethoxy- (No. 11) and *n*-butoxy-acetic (No. 12) esters and even more so with phenoxy-acetic (No. 16). Therefore,

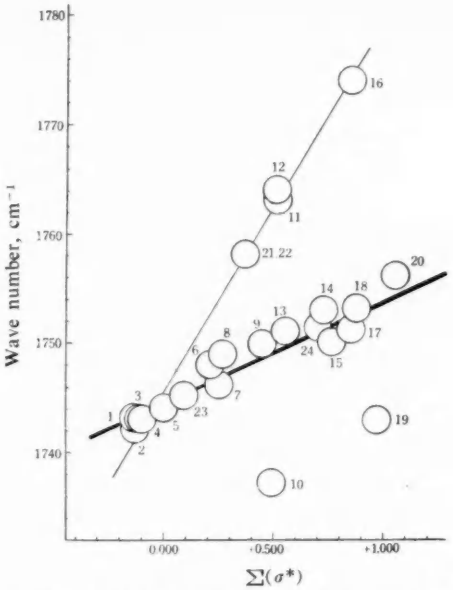


Fig. 1. The linear correlation between polar substituent constants and ester carbonyl frequencies of *p*-bromophenacyl esters.
(The numbers refer to the compounds listed in Table II.)

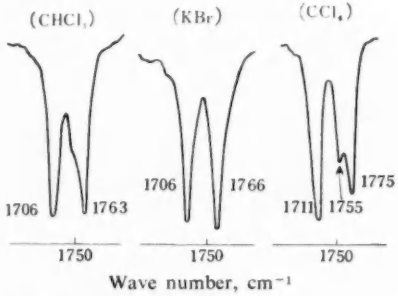


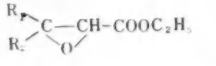
Fig. 2. Infrared spectra of *p*-bromophenacyl ethoxy acetate.

it may be concluded that these deviations are characteristic with esters having an etheric oxygen at their α-positions.

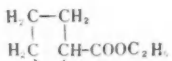
As is shown in Fig. 2, the band of these esters in chloroform solution had a shoulder at a low frequency region, while only a sharp band appeared when the spectrum was measured in the solid state (potassium bromide disks). Recently, House and Blaker[5] have reported that in the carbonyl region glycidic esters such as III and ethyl tetrahydrofuroate (IV) both

3) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **75**, 4231 (1953).
4) R. W. Taft, Jr., in M. S. Newman ed., "Steric Effects in Organic Chemistry", Chapter 13, John Wiley & Sons, Inc., New York (1956).
5) H. O. House and J. W. Blaker, *J. Am. Chem. Soc.*, **80**, 6389 (1958).

exhibited two bands attributable to the presence of two conformations of esters in the solution[6]. The same explanation can be applied to *p*-bromophenacyl esters having an α-oxygen substituent.

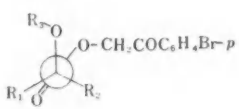


(III)

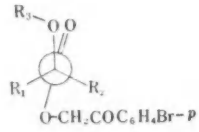


(IV)

These esters would exist in two conformations V and VI in solution. Since the C=O and C-O dipoles are oriented in opposite directions in the conformation V, the spectrum of this structure would be expected to have a normal carbonyl absorption band of *p*-bromophenacyl esters in the range of 1740~1755 cm^{-1}, while in the conformation VI, where these dipoles are oriented in the same direction, the direct field effects between these dipoles would be expected, which would result in the carbonyl vibration shifting towards higher frequencies.



(V)



(VI)

These considerations are exactly parallel with those employed in interpret the infrared spectra of α-haloketones and α-haloesters[7].

The molecular extinctions of the two conformations are not known and the actual concentrations of the two conformations could not be calculated. However, it may be concluded that these esters exist largely as the conformation VI in chloroform solution, since the lower frequency band of the conformation V is a shoulder and since a study of α-bromoketo steroids suggests that the molecular extinction of the conformation VI should have a lower value than that of V[8]. Recently, Brown[9] has reported the value 3.36 : 2.77 for the ratio of apparent intensities of the corresponding conformations for ethyl α-ethoxy acetate.

To explore the validity of the above presumption, infrared spectra of these esters were examined in carbon tetrachloride solution. As was evident from studies[10] of α-bromocyclohexanone in various solvents, the less polar conformation V is stabilized by the less polar solvent so that the spectra of conformations V and VI would be separated from each other. This is actually the case; thus, as is shown in Fig. 2, the spectrum of *p*-bromophenacyl ethoxyacetate in carbon tetrachloride solution exhibits two bands at 1755 and 1775 cm^{-1} in ester carbonyl region corresponding to the conformations V and VI, respectively. The same is true for *n*-butoxyacetic and monochloroacetic esters. The band frequencies of some esters in carbon tetrachloride solution are shown in Table II. Monoiodoacetic ester and α-bromobutyric ester did not exhibit two bands even in this non-polar solvent. This observation agrees with the conclusion of Brown[9] that the distribution of two conformations of these esters is controlled largely by the size of the group rather than by the dipole-dipole repulsion.

Table II. Infrared spectra of *p*-bromophenacyl esters ($RCOOCH_2COC_6H_4Br$-*p*) in carbon tetrachloride solution

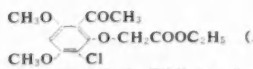
Compound[a] No.[b]	R-	Ester C=O cm^{-1}	Keto C=O cm^{-1}
3	n-C_3H_7-	1753	1712
4	C_2H_5-	1755	1712
5	CH_3-	1759	1712
6	$C_6H_5CH_2$-	1751	1711
8	$CH_3CHClCH_2$-	1753	1711
9	$CH_3CH(OH)$-	1753	1710
10	H-	1745	1713
11	$C_2H_5OCH_2$-	1775, 1755	1711
12	n-$C_4H_9OCH_2$-	1773, 1753	1712
17	ICH_2-	1754	1712
18	CH_3CH_2CHBr-	1755	1711
20	$ClCH_2$-	1781, 1758	1711

a) Most of the compounds not listed in this table were sparingly soluble in carbon tetrachloride and their spectra could not be examined.

b) The number refer to the compounds listed in Table I.

Another peculiarity observed in the spectra of most *p*-bromophenacyl esters was the appearance of a set of three strong to medium intensity bands around 1000 cm^{-1}, which probably originate from the *p*-bromophenacyl

6) Dawkins and Mulholland noticed that the ester carbonyl band of the ester (A) splitted (1763 and 1753 cm^{-1}) even in the solid state (Nujol). See, A. W. Dawkins and T. P. C. Mulholland, *J. Chem. Soc.*, **1959**, 2211.



(A)

7) L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, **1957**, 4294.

8) R. N. Jones, D. A. Ramsay, F. Herling and K. Dobriner, *J. Am. Chem. Soc.*, **74**, 2828 (1952).

9) T. L. Brown, *J. Am. Chem. Soc.*, **80**, 3513 (1958).

10) J. Allinger and N. L. Allinger, *Tetrahedron*, **2**, 64 (1958).

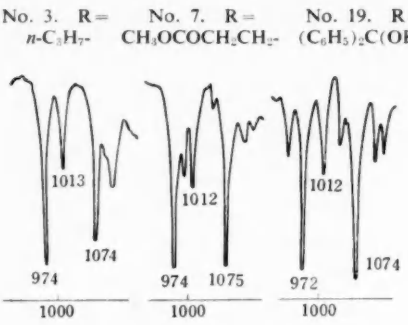


Fig. 3. Characteristic bands of *p*-bromophenacyl ester ($RCOOCH_2COC_6H_4Br$-*p*) around 1000 cm^{-1} ($CHCl_3$).

group. Thus, these bands appear at 1076±2 cm^{-1} (strong), 1014±2 cm^{-1} (medium), and 972±4 cm^{-1} (strong), and are almost independent of the structure of respective acids. These bands are therefore useful for the recognition of *p*-bromophenacyl esters. The characteristic shapes of these bands are shown in Fig. 3.

Provided that direct comparisons of spectra of *p*-bromophenacyl esters with the linear correlation of Eq. 1 are possible, the ester carbonyl absorption band would enable one to evaluate the appropriate $\Sigma\sigma^*$ value, which, in turn, would predict the nature of substituents around the carboxyl group of the respective acid, since only a few anomalies have been observed in the correlation except for those described above. While the abnormal frequency lowering in formic ester (No. 10) is not unexpected, the cause for the considerable deviation from the correlation in benzilic ester (No. 19) is not known.

Finally it is of interest to note that the frequencies of esters having an etheric function at their α-position define another straight line in Fig. 1. Since the abnormally high frequency of these esters is ascribable to the direct field effect of alkoxyl groups, this linear correlation would probably suggest the linearity between the field effect and the inductive effect, at least, for these alkoxyl groups. However, more accurate and sufficient data may be required in order to test such a quantitative correlation.

Experimental

General Procedure for Preparation of *p*-Bromophenacyl Esters. — About 500 mg. of the acid are added to a mixture of 1 ml. of water and 2 ml. of alcohol in a small flask and are neutralized carefully with crystalline sodium bicarbonate. The mixture is warmed very gently on a water bath until evolution of carbon dioxide ceases. The remaining sodium bicarbonate is filtered and the filtrate is added with one or two drops of the acid. Five ml. of alcohol and 500 mg. of *p*-bromophenacyl bromide are added and the mixture is then heated under reflux for 1 hr. Occasionally the addition of a few more milliliters of alcohol may be necessary if a solid separates during the refluxing. The solution is allowed to cool, and the precipitated ester is purified by recrystallization from alcohol or from aqueous alcohol. The melting point of the ester is listed in Table I.

Infrared Absorption Measurements.—The spectra were recorded on a Hilger H 800 double beam instrument equipped with sodium chloride optics. Spectra of the solution were measured using 0.16 mm. sodium chloride cells.

The authors wish to express their gratitude to Dr. Isao Satoda, Nippon Shin-yaku Co. for his interest in this research. They are indebted to the Parke Davis Co. for fellowships to H. N. during the course of the research, and are also grateful for a grant from the Ministry of Education.

Chemical Institute
Faculty of Science
Nagoya University
Chikusa, Nagoya

SHORT COMMUNICATIONS

Proton Magnetic Resonance Absorption of Aluminum Hydroxides and of their Thermal Dehydration-Products

By Tokutaro HAGIWARA and Tatsuo SAITO*

(Received February 29, 1960)

The phase transformations occurring in the thermal decomposition of the alumina trihydrate belong, as of old, to the subject of extensive researches. The present authors have now tried to study the thermal dehydration of alumina trihydrate by means of a method of proton magnetic resonance absorption**.

The starting material here employed was a bayerite prepared by a chemical reaction of an aluminum chloride solution with an aqueous ammonia. Each specimen was subjected to the corresponding heating of this starting material during 3 hr. in the air at 100°, 200°, 220°, 250°, 300°, 450° and 600°C, respectively. They were sealed in the evacuated glass tubes which were pumped out to a high vacuum, either at room temperature during 12 hr. or at 110°C during 6 hr., the latter having the purpose of an after-treatment. We call the former group as "a-series" and the latter one as "b-series".

For the NMR measurements, we have used the a.c. modulation technique of the magnetic field at the d.c. magnetic field of about 3100 gauss. The detecting apparatus has the ordinary constitution, which is composed of an autodyne oscillator, an audio-frequency amplifier, a lockin-amplifier and a recording milliammeter.

The measurements of the proton magnetic resonance were also made in the well-known definite hydrargillite, bayerite, böhmite and natural diaspore, respectively. Some reproductions of the experimental line shapes of the proton resonances are shown in Figs. 1 and 2.

As is seen in Fig. 1, the line shapes of the hydrargillite and of the bayerite or the starting material may be presumably understood as being composed of two parts: one is situated at the center with the narrower width and another is of very broad at both sides of it. The line shape of the böhmite shows the signal of the three spin type, while that of the

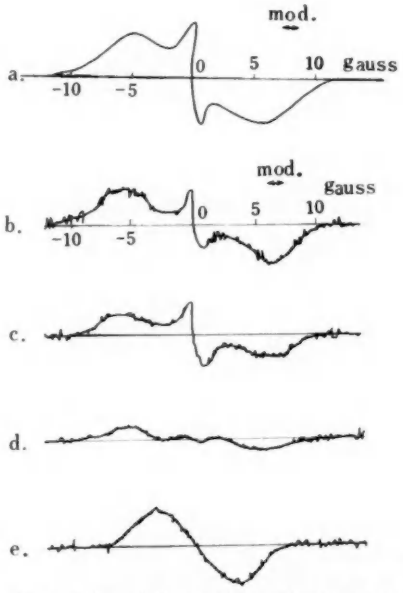


Fig. 1. Recorded derivatives of proton resonance in the starting material and the known, definite hydroxides.
a: Starting material b: Hydrargillite
c: Bayerite d: Böhmite e: Diaspore

TABLE I. THE VALUES OF THE SECOND MOMENTS CALCULATED FROM THE EXPERIMENTAL DERIVATIVES

Specimen	Second moment (in gauss^2)
Starting material	12.9
Bayerite	13.1
Hydrargillite	15.2
Böhmite	14.0
Diaspore	6.3
Dehydrated at 100°C-(b)	13.4
〃 at 200°C-(b)	13.7
〃 at 220°C-(b)	14.0
〃 at 250°C-(b)	8.3
〃 at 300°C-(b)	6.8
〃 at 450°C-(b)	4.3
〃 at 600°C-(b)	3.0

* Present address; Government Chemical Industrial Research Institute, Tokyo, Honmachi 1-chōme, Shibuya-ku, Tokyo.

** Presented partly at the Symposium on Structural Chemistry, Osaka, Oct. 31, 1954.

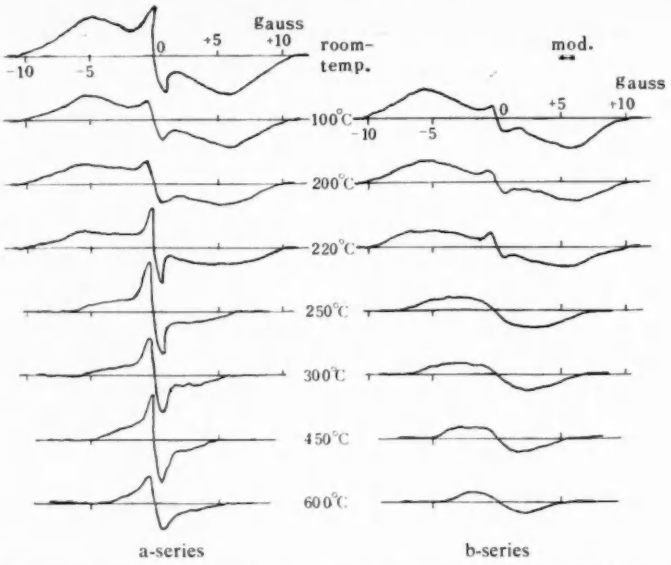


Fig. 2. Recorded derivatives of proton resonance in the a- and b-series—(without and with the after-treatments, in vacuo, 110°C).

diaspore shows the single and narrow line. The values of the second moments calculated from the experimental derivative curves are shown in Table I.

The line shapes of each specimen dehydrated at 100° and 200°C are both similar to that of the starting material. The amplitudes of the central components observed for these line shapes are somewhat reduced by the thermal after-treatment, as in a high vacuum pumping at 110°C, but they yet never disappear by such a treatment. Nevertheless, the line shapes of the specimens dehydrated at about 220°C and higher make quite a difference from above two specimens and the height of the central peaks in these line shapes considerably increases. It is noteworthy that these central peaks, however, disappear by the such after-treatment, as in a high vacuum pumping at 110°C. These interesting behaviors can be seen in Fig. 2. Therefore, we are to suppose that these central peaks in the latter case originate from the water-molecules which are adsorbed by the decomposed products and are in the thermal motion.

Based upon the above experimental fact, the following conclusions can be drawn:

1) The decomposition of this starting material does not occur till the thermal dehydration temperature of about 200°C. This is ascertained in our NMR experiments.

2) The sudden and considerable variation of the central part observed in the line shapes at an about 220°C and higher, seems to show that the first dehydration process of this starting material brings forth an active lower hydroxide, exhibiting very high activity for an adsorption.

3) The gradual decrease of the line width occurring in the range from about 250 to 600°C might be regarded as a result due to the changing of the mixed ratio of the lower hydroxide and alumina phases.

These conclusions will be ascertained by the additional experiment by means of X-ray diffraction method which is in progress in our laboratory.

The authors wish to express their sincere thanks to Professor Tunahiko Shidei and Assistant Professor Syukuro Yano in Kyoto University, under whose continual advice and encouragement the present experiments has been carried out, and also for their so kindness as to allow us the loan of their equipments and the technique throughout this study. This study also has been partly supported under the Scientific Research Expenditure from the Ministry of Education.

Department of Chemistry
Faculty of Science
Hiroshima University
Hiroshima

Thermal Isomerization of 2-Thenylthiocyanate

By Kensuke Takahashi, Tyo Sone,
Yasuo Matsuki and Genjiro Hazato

(Received March 12, 1960)

During the studies of the structural investigation and the identification of thenyl derivatives by means of the NMR technique, we happened upon the occurrence of the thermal isomerization of 2-thenylthiocyanate at about 150°C.

Resonance was observed at 40 mc, the apparatus and the procedure were similar to those previously described[1], and in every sample, cyclohexane was used as an internal reference. The spectrum of the raw product synthesized from thiophene by the procedure of thiocyanomethylation, is shown in Fig. 1a. The lines coming from the aromatic hydrogens in thiophene ring spread over the range of about 20 cps at the low-field side of the spectrum. At the high-field side two lines at 107.5 and 125 cps, referred to cyclohexane signal, are assumed to be the lines coming from the hydrogens of the methylene group. We had expected formerly to be observed only one line coming from this group; whereas, the experimental result showed that the methylene peak was divided into two lines, corresponding to two isomers respectively. After this measurement, the sample was heated at about 150°C for two hours by immersing in a constant temperature bath. In the spectrum of the heated sample, the two lines coming from the methylene hydrogens were found at the same positions but there was a marked difference in their intensities as compared with the non-heated sample, as shown in Fig. 1b. This result indicates the occurrence of a thermal isomerization between two compounds of which our synthesized product consists. The thermal isomerization in allylthiocyanate was firstly shown by Gerlich[2]. Here we have studied the benzyl thiocyanate which shows the thrmal isomerization at about 250°C, reported already by Hennicke[3]. Its spectrum shows two lines coming from methylene and aromatic hydrogens at 96 and 229 cps, referred to cyclohexane signal, respectively. By heating of this compound at about 150°C for two hours, no change of its NMR spectrum was observed in comparison with 2-thenyl derivative, but after heating at about 250°C for two hours, the line coming from the methylene group was found at 111 cps with the other small neighboring peaks, and the lines of the aromatic hydrogens were found at 224 and 228 cps. This phenomenon is assumed as the isomerization from thiocyanate to isothiocyanate which is promoted by heating, the same is the case with that observed in 2-thenyl derivative. The isomerization in question here observed in the NMR spectrum is represented by the shift of the line coming from the methylene group to the lower field, which is attributed to the change of the electronegativity and of the second-order high frequency paramagnetism of the adjacent group. The detailed result on the thiocyanomethylation of thiophene will be published in the Journal of the Chemical Society of Japan, Ind. Chem. Sec.

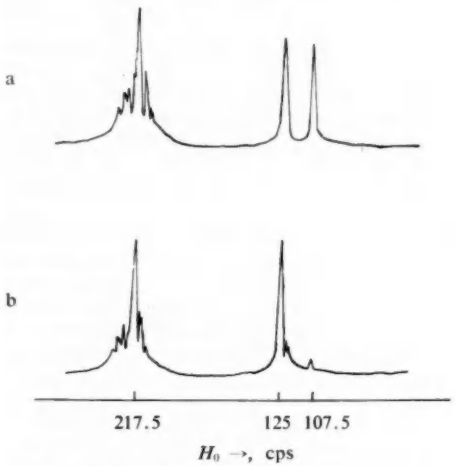


Fig. 1. The proton magnetic resonance spectra of the raw product synthesized from thiophene by thiocyanomethylation. (a) before heating; (b) after heating at about 150°C for two hours. Applied magnetic field increasing from left to right.

The Chemical Research Institute of Non-aqueous Solutions
Tohoku University
Katahira-cho, Sendai

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On the Electronic Structure of Thiothiophten

By Kôgorô MAEDA

(Received June 10, 1960)

Recently the structure of a thiothiophten molecule was clarified through the X-ray analysis by Bezzi, Mammi and Garbuglio[1], who proposed a condensed ring system characterized by no-bond resonance structure. On the basis of this peculiar structure, Giacometti and Rigatti[2] have made simple LCAO treatment on the superimposed σ and π systems of nonlocalized electrons in thiothiophten, by using only p type orbitals for valence states of sulfur atoms. However, since the system involving no-bond resonance structure is somewhat unlikely to occur, an alternative interpretation on the electronic structure of thiothiophten will be given in the present report.

It is possible that a $3p$ electron of the sulfur atom is promoted to a $3d$ orbital and interacts with other $3p$ electrons through *pd* hybridization[3]. Then it may be reasonable to consider that the central sulfur atom in the straight bond S-S-S of thiothiophten is in a valency state capable of forming the σ skeleton of bonds through the *pd* hybridization. The expected valency state of the central sulfur atom would be in the electron configuration $3s^2 3p^3 3d$; one of $3p$'s, $3p_x$, hybridizes with a $3d$ orbital, going to make up the σ bonds of S-S-S in the linear arrangement, and $3p_y$ is adopted to form a C-S σ bond with one of sp^2 orbitals of the neighboring central carbon atom. These configurations can account for both the so-called abnormal length of the bond between two sulfur atoms[3-5] and the right angle of S-S-C with respect to the central sulfur atom. Thus it might be said that the full σ skeleton of the condensed ring system of thiothiophten is composed of the bonds obtained above through the hybridization and other C-S and C-C bonds without introducing the no-bond resonance structure. Over this σ ring system covers the π electron conjugation system, in which the remaining $3p$ orbital, namely the $3p_z$ orbital participates. The electronic structure of thiothiophten can now be treated according to the usual LCAO approximation without considering the σ skeleton.

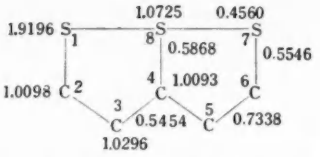

Fig. 1. Molecular diagram of thiothiophten.

In Fig. 1 are given the results obtained by the simple LCAO π approximation on thiothiophten. In calculating the molecular diagram, the following assumptions were adopted: All the Coulomb intengrals were taken to be equal to the common value (so-called α_c) except for two sulfur atoms S_1 and S_7 (see Fig. 1), for which a value less by 0.2β was applied, because the equivalent conjugation systems of thiothiophten in terms of valence bond method are liable to make the atoms positively charged[6]. Furthermore Longuet-Higgins' idea was employed for the two atoms[7]. With respect to the exchange integrals, the standard of the value, β was used for all C-C bonds. For S-S and central C-S bonds were given the values 0.3β and 0.6β, respectively, which are both found in the report of Giacometti and Rigatti[2]. The results given in Fig. 1 are those obtained when the exchange integral of C-S involving S_1 or S_7 bears the same value as that of C-C. The employment of the value is due to non-symmetrical character between the two bonds on the sulfur atom.

The results obtained in this paper are almost the same as those of Giacometti and Rigatti[2], but they are not necessarily the best. It must be noticed, however, that the results obtained without the help of no-bond resonance idea are appropriate at any rate, although many approximations were necessary in the calculation. The insufficient character of the results may be due to the inadequate values of parameters, which should be determined to predict correctly the values of the dipole moment and resonance energy[6]. Details will be further discussed in subsequent publications.

Electrotechnical Laboratory
Tanashi P. O., Tokyo

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Hydration of Thujopsene to Widdrol

By Shizuo NAGAHAMA

(Received August 18, 1960)

Hydration of thujopsene was first reported by Tanaka and Yamashita[1], who obtained an alcohol $C_{15}H_{26}O$, m. p. 120~122°C, $[\alpha]_D$+115.3° (yield 6%) under mild Bertram-Wahlbaum condition.

In the course of studies on the acid catalyzed isomerization of thujopsene, it was found that thujopsene gave another alcohol which was identified as widdrol by direct comparison with the sample obtained by Erdtman and Thomas[2].

A mixture of oxalic acid (50 g.), water (50 cc.), ethanol (600 cc.) and thujopsene (100 g.) was refluxed for 10 hr. The highest boiling fraction of the reaction products (b. p. 124~129°/5mmHg, 25 g.) solidified on standing and repeated recrystallization of this material from petroleum ether and sublimation under reduced pressure gave widdrol, m. p. 98°C, $[\alpha]_D$+105° (c=0.87), $C_{15}H_{26}O$ (Found: C, 81.02, H, 11.79%). The hydrocarbon fraction (b. p. 105~114°C/5 mmHg, 65 g.) was treated under the same condition as mentioned above and further 4 g. of crude widdrol was obtained. The hydrocarbon fraction (b. p. 104~111°C/5 mmHg, 41 g.) recovered from this reaction mixture underwent the same treatment further to give the product; b. p. 113~114°C/5mmHg, n_D^{30} 1.5022, d_4^{30} 0.9251, $[\alpha]_D$+22.2° (neat), I. R. bands 1638, 888 cm^{-1} (17 g.).

The author wishes to express his gratitude to Professor H. Erdtman and Dr. C. Enzell for kind offer of the precious natural widdrol. He also appreciates the kind guidance of Professor S. Akiyoshi.

Department of Organic Synthesis
Faculty of Engineering
Kyushu University
Hakozaki, Fukuoka

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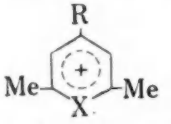
Non-benzenoid Aromatic Heterocycles. II[1]. *Reaction of Pyrylium Salt with Potassium Hydrosulfide*

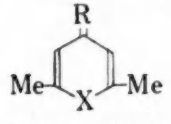
By Hiroshi KATO, Takatoshi OGAWA and Masaki OHTA

(Received August 20, 1960)

In the preceding paper[1], the conversion of 2, 6-dimethyl-4-methoxypyrylium salt (Ia) into 4-pyrone derivatives on treatment with sodium salts of active methylene compounds has been described. In the present communication, the reaction of this type with potassium hydrosulfide on 2, 6-dimethyl-4-methoxypyrylium perchlorate (Ia) is reported. When pyrylium salt Ia was treated with potassium hydrosulfide at room temperature, attack at the 4 position and removal of methoxyl group took place, and 2, 6-dimethyl-4-thiopyrone (IIa) was obtained. When this reaction was carried out under reflux and under a current of hydrogen sulfide, substitution of sulfur atom to both the 1 and 4 positions occurred, and 2, 6-dimethyl-1-thia-4-thiopyrone (IIb) was obtained. These compounds (IIa and IIb) have so far been prepared respectively by treating 2, 6-dimethyl-4-pyrone (IIc) with phosphorus pentasulfide[2], and by treating 2, 6-dimethyl-4-thiopyrone (IIa) with potassium hydrosulfide[3]. In the absence of hydrogen sulfide, the product was a mixture of the above two compounds. Starting from 2, 6-dimethyl-4-methylmercaptopyrylium perchlorate (Ib), 2, 6-dimethyl-1-thia-4-thiopyrone (IIb) was also obtained by the same method. An attempt to prepare 2, 6-dimethyl-4-pyrone (IIc) and -1-thia-4-pyrone (IId) by the action of potassium hydroxide on 2, 6-dimethyl-4-methylmercaptopyrylium (Ib) and -1-thiapyrylium perchlorate (Ic), respectively, was unsuccessful. This result is in agreement with the report of King[4] on



Ia : R=OMe, X=O
Ib : R=SMe, X=O
Ic : R=SMe, X=S



IIa : R=S, X=O
IIb : R=S, X=S
IIc : R=O, X=O
IId : R=O, X=S

1) Part I: M. Ohta and H. Kato, This Bulletin, **32**, 707 (1959).
2) L. C. King et al., *J. Am. Chem. Soc.*, **73**, 300 (1957).
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4) L. C. King et al., *J. Org. Chem.*, **20**, 448 (1955).

the order of ease of replacement of methoxyl and methylmercapto group, and with the observation of the present author in the preceding paper[1], where the methylmercapto group is reported to be not mobile.

Experimental

2, 6-Dimethyl-4-thiopyrone (IIa).—Into a suspension of Ia (5 g.) in methanol was added a methanol solution of potassium hydrosulfide (prepared from 5 g. of potassium hydroxide) at room temperature and with stirring. After an hour, the mixture was acidified with conc. hydrochloric acid and was poured into an aqueous solution of sodium bicarbonate. The precipitate (4.3 g., m. p. 144°C) was recrystallized from ethanol affording yellow needles (2 g.), m. p. 145°C. No m. p. depression occurred on admixture with an authentic specimen[2].

2, 6-Dimethyl-1-thia-4-thiopyrone (IIb).—Into a suspension of Ia (10 g.) in methanol was added a methanol solution of potassium hydrosulfide (prepared from 10 g. of potassium hydroxide) under a current of hydrogen sulfide and under reflux and stirring. After an hour, the mixture was treated by the above method and the precipitate (6.1 g., m. p. 106~119°C) was recrystallized from ligroin affording red needles, m. p. 116~117°C* (Found: C, 54.33; H, 5.56%).

The same compound was obtained starting from Ib by the same method (yield, poor).

When Ia was refluxed with potassium hydrosulfide in the absence of hydrogen sulfide, the product (1.7 g., m. p. 102~103°C) was a mixture of IIa and IIb (Examined by micro m. p. determination apparatus: The mixture consists of yellow needles (IIa) and red needles (IIb), and these compunds melted at their respective melting points.), the separation of which by recrystallization or by chromatography (alumina-benzene) was very troublesome.

Action of Potassium Hydroxide on Ib and Ic.—When Ib or Ic was treated with potassium hydroxide in methanol, a small amount of hydrogen sulfide was evolved, but the product was an unpurifiable resinous substance.

The authors are indebted to Mr. Asaji Kondo for performing the microanalyses.

Laboratory of Organic Chemistry
Tokyo Institute of Technology
Meguro-ku, Tokyo

* Reported m.p.[3] 116~117°C.

Non-benzenoid Aromatic Heterocycles. III[1]. *Conversion of 4-Pyrone Derivatives into 4-Pyridone Derivatives*

By Hiroshi KATO, Takatoshi OGAWA and Masaki OHTA

(Received August 20, 1960)

In the first paper of this series[2], the condensation of active methylene compounds with 2, 6-dimethyl-4-pyrone has been reported. In the present communication, the action of amines on these condensation products is described. These compounds are similar to pyrone in their electronic structure, and it is of interest to examine if these compounds are converted into the corresponding pyridone derivatives like pyrones. If the reaction takes place, it will be a valuable route to many pyridone derivatives. As model compounds, 4-(dicyanomethylene)-2, 6-dimethyl-4*H*-pyrane (Ia) and 4-(ethoxycarbonylcyanomethylene)-2, 6-dimethyl-4*H*-pyrane (Ib) were selected. With Ia, the reaction with amines (aniline, benzylamine, hydrazine hydrate) took place and gave the corresponding *N*-substituted 4-(dicyanomethylene)-2, 6-dimethyl-1, 4-dihydropyridines (IIa-c). As to the structure of the reaction product with hydrazine hydrate, two structures, IIc and III, are possible, but the *N*-aminopyridone structure (IIc) was established by condensing it with benzaldehyde to form the benzal derivative (IIg). Although Ia did not react with ammonium chloride, it was converted into pyridone derivative (IId) by heating it in formamide. Of special interest is IId, since it may be isomerized to pyridine derivative IV and would afford a valuable route to many pyridine derivatives*.

Starting from Ib, the corresponding pyridone derivatives (IIe, f) were prepared with benzylamine and hydrazine hydrate, but with aniline or formamide, the starting material was recovered unchanged. It may be worth while to note that the ester group of Ib did not suffer amminolysis.

An attempt to prepare 1-thiapyrone derivatives by treatment of Ia and Ib with potassium hydrosulfide was not successful.

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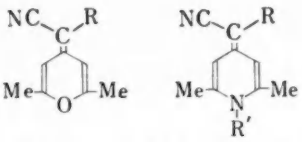
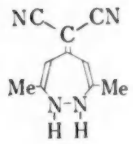
* After the completion of this work, a review on pyrylium salt by Dimorth[3] appeared, where he briefly reported that he also attempted the reaction of this type and obtained the corresponding pyridine derivatives.
3) K. Dimroth, *Angew. Chem.*, 72, 331 (1960).

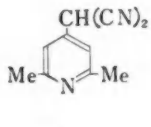


Ia : R=CN
Ib : R=COOEt

IIa : R=CN, R'=Ph
IIb : R=CN, R'=$PhCH_2$
IIc : R=CN, R'=H_2N
IId : R=CN, R'=H
IIe : R=COOEt, R'=$PhCH_2$
IIf : R=COOEt, R'=H_2N
IIg : R=CN, R'=N=CHPh



III



IV

Experimental

Reaction of Ia or Ib with Amines.—**IIa,** A mixture of Ia (3.5 g.) and an excess of aniline (4 g.) was gently refluxed for an hour. The reaction mixture was washed with dil. hydrochloric acid and the residue (1.0 g., m. p. 310~313°C) was recrystallized from acetic acid giving white needles, m. p. 314~315°C. Yield 20%.

Found: N, 17.11. Calcd. for $C_{16}H_{13}N_3$: N, 16.99%.

Similarly, the following compounds were obtained:

IIb, (from Ia and benzylamine; heated at 150°C.) yellow needles (recrystallized from ethanol) m. p. 242~245°C. Yield 34%.

Found: N, 16.28. Calcd. for $C_{17}H_{15}N_3$: N, 16.08%.

IIc (from Ia and hydrazine hydrate; heated at 100°C) white needles (recrystallized from acetic acid) m. p. 291~292°C (decomp.) Yield 40%.

Found: N, 30.36. Calcd. for $C_{10}H_{10}N_4$: N, 30.09%.

IIe, (from Ib and benzylamine) white needles (recrystallized from ethanol) m. p. 183~184°C. Yield 80%.

Found: N, 9.15. Calcd. for $C_{19}H_{20}O_2N_2$: N, 9.09%.

IIf, (from Ib and hydrazine hydrate) pale yellow needles (recrystallized from ethanol) m. p. 217~218°C. Yield 71%.

Found: N, 17.70. Calcd. for $C_{12}H_{15}O_2N_3$: N, 18.02%.

N-Benzalamino-4-(dicyanomethylene)-2,6-dimethyl-1,4-dihydropyridine (IIg),—A solution of IIc (0.6 g.) and benzaldehyde (0.4 g.) in acetic acid was refluxed for an hour, and then diluted with water and the precipitate that separated out was collected (0.6 g., m. p, 254~255°C). Recrystallization from acetic acid afforded yellow needles, m. p. 294~295C°.

Found: C, 74.21; H, 5.25; N, 20.00. Calcd. for $C_{17}H_{14}N_4$: C, 74.43; H, 5.14; N, 20.43%.

4-(Dicyanomethylene)-2,6-dimethyl-1,4-dihydropyridine (IId).—A solution of Ia (5 g.) in formamide (5 g.) was heated at 150°C for an hour. The crystals which separated out on cooling were collected (1.7 g., m. p. 280~300°C) and recrystallized from formic acid giving yellow needles, m. p. 330~331°C.

Found: C, 70.37; H, 5.36; N, 24.44. Calcd. for $C_{10}H_9N_3$: C, 70.15; H, 5.30; N, 24.55%.

Reaction of Potassium Hydrosulfide with Ia or Ib,—When Ia or Ib was refluxed in methanol solution of potassium hydrosulfide, the starting material was recovred unchanged.

The authors are indebted to Mr. Asaji Kondo for performing the microanalyses.

Laboratory of Organic Chemistry
Tokyo Institute of Technology
Meguro-ku, Tokyo

Studies on Metal Complex Species Using an Anion Exchange Resin. I. Derivation of Equations and Application to Mercury(II)-Nitrate Complex

By Hirohiko WAKI

(Received July 16, 1960)

A generalized equation for determining the composition of metal complex species was derived by introducing the complex formation equilibrium in the resin phase, which has not been considered formerly.

When most part of a metallic element exists in the form of MX_m^{a-bm} in the solution phase and MX_n^{a-bn} in the resin phase as a result of complex formation between the metal ion M^{a+} and the anion X^{b-}, the following equation may be derived:

$$\log D = (n - a/b) \log [X^{b-}] - (m - a/b) \log (X^{b-}) + K + G \qquad (1)$$

where D represents the distribution coefficient of the metallic element, ( ) and [ ] indicate the concentrations in the solution phase and the resin phase, respectively, and K and G the terms containing the complex formation constant and the activity coefficient in both phases. Under the condition in which K and G are constant,

$$\frac{d\{\log D+(m-a/b)\log(X^{b-})\}}{d\log[X^{b-}]}=n-a/b \quad (2)$$

$$\frac{d\{\log D-(n-a/b)\log[X^{b-}]\}}{d\log(X^{b-})}=-(m-a/b) \quad (3)$$

Accordingly, when m is known and D, (X^{b-}) and $[X^{b-}]$ are measurable, n can be determined graphically, and m is also obtained when n is known. Even if both are unknown, one of them can be determined when either (X^{b-}) or $[X^{b-}]$ is kept constant. Although it is practically impossible to set a condition in which the activity coefficient term is strictly constant, that may be roughly realized when a small quantity of the metallic element is used and the ionic strengths in the two phases are each kept constant by the addition of an indifferent anion, and therefore the complex form may be determined through measurements in the range where the predominant anionic species is X^{b-}.

As an application of these equations, adsorption of mercury(II) from a sodium nitrate solution was studied by means of $NaNO_3$+$NaClO_4$ mixed medium, where Hg^{2+} was employed as M^{a+}, NO_3^- as X^{b-} and ClO_4^- as an additional anion. Assuming that mercury is present as Hg^{2+} in a sodium nitrate solution acidified by nitric acid, Eq. 1 is obtained simplified as follows:

$$\log D-2\log(NO_3^-)=(n-2)\log[NO_3^-]+K+G \quad (4)$$

The experiment was carried out by equilibrating 2 g. of an anion exchanger "Dowex 1-X8" (100~200 mesh) of nitrate form with a mixed solution containing 0.1 millimole of mercury(II) nitrate, 0.5 millimole of nitric acid, and a series of mixtures $NaNO_3$+$NaClO_4$ of various mixing ratios (total concentration is 3 M or 5M), followed by determination of mercury in the solution and nitrate in the resin. Mercury in the resin and nitrate in the solution were determined by subtraction since their total amounts are known. The distribution coefficient of mercury was calculated as

$$D=\frac{\left(\begin{array}{c}\text{millimole of Hg adsorbed per}\\ \text{milliequivalent of resin}\end{array}\right)}{\left(\begin{array}{c}\text{millimole of Hg per}\\ \text{milliliter of solution}\end{array}\right)}$$

The ion concentrations in the resin phase were always represented as millimole of the ion per milliequivalent of the resin.

Log $D-2\log(NO_3^-)$ was plotted against logarithm of the nitrate ion concentration in the resin, as shown in Fig. 1. The curves show linearity and their slopes correspond to $n=3.8$ for both cases of 3 M and 5 M of the external total concentration. Accordingly, it may be recognized that most mercury(II) is adsorbed in the form of $Hg(NO_3)_4^{2-}$ from the acidified 3~5 M sodium nitrate solution.

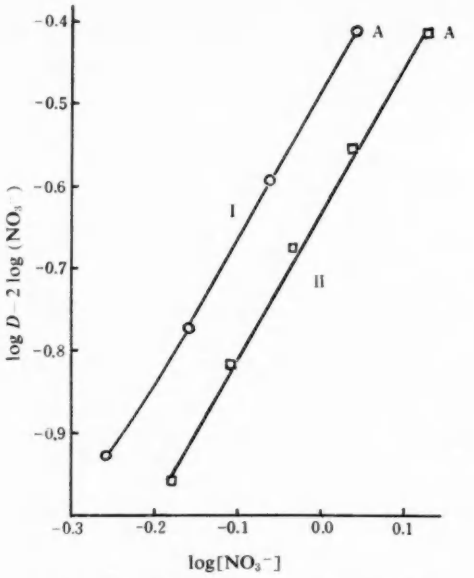


Fig. 1. Distribution coeficient of Hg(II) as a function of the nitrate concentration in the resin phase.
The measurements were carried out at the nitrate-rich range. A is the point in the absence of perchlorate.
I. Total concentration of the external solution is 3 M
II. 〃 5 M

It may also be possible that the lower complex species, such as $Hg(NO_3)^+$ or $Hg(NO_3)_2^0$, exist in the solution. However, since the degree of change in nitrate concentration in the solution phase was much smaller than that in distribution coefficient, the change of the second term on the right side in Eq. 1 may slightly affect the conclusion. Details of this investigation will be reported later.

The author wishes to express his sincere thanks to Professor J. Yoshimura of Kyushu University for his suggestion and encouragement.

Department of Chemistry
Faculty of Science
Kyushu University
Hakozaki, Fukuoka

Synthesis of Isokinetin, 2-N-furfurylaminopurine and its Leaf-growth Activity (Studies of Isokinetin and its Analogs. Part I)

By F. Shigeo Okumura, Hiroshi Kusaka and Tetsuji Takematsu

(Received July 11, 1960)

More than fifty kinetin-analogs which belong to 6-(*N*-substituted)-aminopurine, have been prepared and it was found[1] that some of them have a leaf-growth stimulating activity. During the course of this study, our interest was directed to investigate whether the leaf-growth activity is still retained after the furfurylamino group at 6-position of the purine ring migrates to the 2-position.

After making many unsuccessful attempts to synthesize 2-(*N*-furfuryl)-aminopurine, we succeeded in preparing this new compound by the process outlined in Fig. 1.

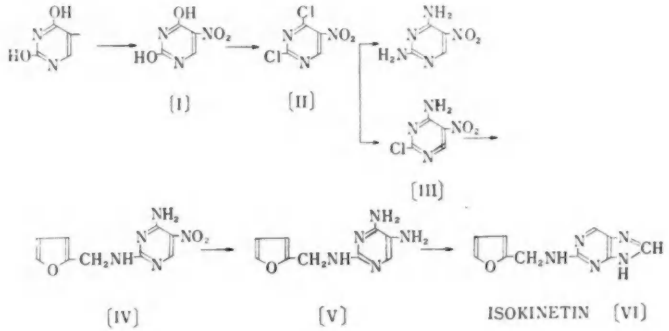
Nitration of uracil with fuming nitric acid gave 2, 6-dihydroxy-5-nitropyrimidine (I) in 90.7% yield, m. p. 294~295°C (Found: N, 26.70. Calcd. fo. $C_4H_3N_3O_4$: N, 26.75%). This was chlorinated with phosphoroxychloride in the presence of dimethylaniline to give 2, 6-dichloro-5-nitro-pyrimidine (II) in 64% yield.

Amination of II by ammonia in methanol-ether solution gives the mixture of 2, 6-diamino-5-nitro-pyrimidine and 2-chloro-6-amino-5-nitro-pyrimidine (III). However, III can be obtained in 60% yield when amination takes place at low temperature (below 0°C), m. p. of III, 220~221°C, Found: N, 31.95. Calcd. for $C_4H_3N_4O_2Cl$: N, 32.10%. III was then converted into 2-furfurylamino-6-amino-5-nitropyrimidine (IV) in 69.7% yield by refluxing with furfurylamine for 3~4 hr. (m. p, 159~160°C, Found: N, 29.50. Calcd. for $C_9H_9N_5O_3$: N, 29.76%).

IV was finally reduced catalytically with Raney nickel in methanol to give 2-furfuryl-amino-4, 5-diaminopyrimidine (V) which was refluxed with formamide yielding 2-(*N*-furfuryl)-aminopurine (VI) in 24% yield. Tan-colored needle from absolute alcohol, m. p. 195~196°C, (Found: C, 55.88; H, 4.01; N, 32.55. Calcd. for $C_{10}H_9N_5O$: C, 55.55; H, 4.67; N, 32.37%). The ultraviolet spectrum of isokinetin showed almost the same absorption as that of kinetin.

The leaf-growth activity of isokinetin was compared with that of kinetin by using *Rhaphanus cotyledon* by the Takematsu method[2]. The 200 mg./l. solution of kinetin or isokinetin was sprayed by using 0.4 ml. microsprayer on both sides of *Rhaphanus cotyledon*, which was cultured on the sand for 4 days at 15~18°C after coming out the *cotyledon* of *Rhaphanus sativa*. The increase of the leaf-area was measured 5 days after spraying. Isokinetin stimulates leaf-growth, but activity was observed to be about 80% of that of kinetin.

Okumura and Kuraishi[3] observed that kinetin inhibits the growth of the root of *Brassica chinensis L var. amplexicaulis Makino* at the concentration of 10^{-3}mg./l. In the present communication we have observed the same inhibiting action of both kinetin and isokinetin against the growth of roots of *Rhaphanus sativa* and *Brassica juncea*. Kinetin inhibited the growth of roots remarkably, even in the concentration of 5mg./l. but the inhibiting action of isokinetin was observed only at the concentration of 50 mg./l. or higher. As gibberelline and indol acetic acid has no inhibitory



1) F. S. Okumura et al., This Bulletin, **30**, 194 (1957); **32**, 886, 889, (1959).

2) Method of *Rhaphanus* test and its application, by T. Takematsu (1959).

3) Unpublished work.

effect against the growth of plant roots, this inhibiting action is specific for the kinetin and isokinetin groups.

From the above observation it is clear that there are some interesting relationships between the leaf-growth and root-inhibition among the kinetin and isokinetin groups. Concerning this aspect, further studies are now in progress.

Department of Chemistry
University of Tokushima
Tokushima (F. S. O.)

Onoda Cement Co.,
Yamaguchi (H. K.)

Department of Agriculture
University of Utsunomiya
Utsunomiya (T. T.)